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Evaluation of the Generation and Release of Flammable Gases in Tank 241-SY-101

H. Babad
G. D. Johnson
J. A. Lechelt
D. A. Reynolds
Westinghouse Hanford Company

L. R. Pederson
D. M. Strachan
Pacific Northwest Laboratory

D. Meisel
C. Jonah
Argonne National Laboratory

E. C. Ashby
Georgia Institute of Technology

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EVALUATION OF THE GENERATION AND RELEASE
OF FLAMMABLE GASES IN TANK 241-SY-101

ABSTRACT

Tank 241-SY-101 is a double shell, high-level waste tank located in the 200 West Area of the Hanford Site. This tank contains about 1 million gallons of waste that was concentrated at the 242-S Evaporator. Shortly after the waste was put in the tank, the waste began to expand because the generation of gases. In 1990 this tank was declared to have an unreviewed safety question because of the periodic release of hydrogen and nitrous oxide.

A safety program was established to conduct a characterization of the waste and vented gases and to determine an effective means to prevent the accumulation of flammable gases in the tank dome space and ventilation system. Results of the expanded characterization conducted in fiscal year 1991 are presented. The use of gas chromatographs, mass spectrometers, and hydrogen-specific monitors provided a greater understanding of the vented gases. Additional instrumentation placed in the tank also helped to provide more detailed information on tank temperatures, gas pressure, and gas flow rates.

An extensive laboratory study involving the Westinghouse Hanford Company, Pacific Northwest Laboratory, Argonne National Laboratory, and the Georgia Institute of Technology was initiated for the purpose of determining the mechanisms responsible for the generation of various gases. These studies evaluate both radiolytic and thermochemical processes. Results of the first series of experiments are described.

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1.0 INTRODUCTION

Flammable gas generation in tank 101-SY is a top priority waste tank safety issue at Hanford because average peak concentrations above the lower flammability limit (LFL) for hydrogen occur periodically. Such venting of gases is expected to keep reoccurring until some form of remediation is taken. In addition, it is likely that a greater-than-LFL concentration exists at times within the waste. In the unlikely event an ignition source were present during these periods, a hydrogen burn or explosion could occur with a possible release of nuclear waste to onsite and offsite personnel.

Scenarios of significant concern associated with waste in this tank include the following:

- The potential for ignition of flammable gases such as hydrogen-air and/or hydrogen-nitrous oxide

- The potential for secondary ignition of organic-nitrate mixtures on the crust initiated by the burning of flammable gases or a mechanical in-tank energy source.

Administrative and technical controls are in place to restrict activities that could cause undesirable reactions. Nonsparking tools and use of electrical bonding and grounding techniques are used. So-called "normal" activities for tanks of concern are limited to surveillance. Special safety analysis documents prepared for all work inside the tank are extensively peer reviewed and require U.S. Department of Energy (DOE) approval.

Analyses conducted on several samples of crust material have shown that the crust is quite moist, contains a relatively low total organic carbon and does not exhibit significant exothermic behavior. Thus, "crust burn" does not appear to be an issue. A detailed report on this subject will be issued in fiscal year 1992.

A significant portion of the activities of the Waste Tank Safety Program has been directed at the characterization of the gases that are released from the tank and at the determination of the mechanism for the production of the gases. The purpose of this report is to provide a summary of (1) the methods used for characterization of the gas release events, (2) the data obtained from the recent events, and (3) the results obtained from laboratory studies directed at understanding the mechanisms for the formation of the gases.

Although 22 other tanks are also suspected of potentially containing smaller accumulations of hydrogen or other flammable gases, this report focuses only on Tank 241-SY-101. There is a significant difference in significance between Tank 241-SY-101 and the other 22 tanks. Evidence of gas

release, surface level behavior, and knowledge of the other tank contents suggests a much lower likelihood of potentially dangerous gas concentrations in these other tanks.

2.0 BACKGROUND INFORMATION ON TANK 241-SY-101

Construction on Tank 241-SY-101 was completed in 1976. The first waste put into the tank was from the first double-shell slurry campaign using the 242-S Evaporator in 1977. Double-shell slurry is the most concentrated material that the evaporators can produce. The degree of evaporation is limited only by the pumpability of the slurry. One hundred inches of this material was pumped into Tank 241-SY-101.

From 1977 to 1980, the tank received complexed concentrate waste, which was placed in the tank at three different times (Table 1 shows the filling history). A total of 203 in. of complexed concentrate waste was placed on top of the heavier double-shell slurry. Complexed concentrate is a waste from the cesium/strontium recovery process in B Plant. It is rich in complexants such as ethylenediaminetetraacetic acid (EDTA), N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), citric and hydroxyacetic acid. These soluble organics were concentrated with the waste stream to a high total organic carbon.

The last material put into Tank 241-SY-101 was from another campaign of double-shell slurry in the fall of 1980. About 84 in. was put into the tank, which brought the final volume to 387 in. Purge water totaling 8,000 gal was added to the tank between September 1984 and May 1988.

The average estimated composition of Tank 241-SY-101 is provided in Table 2.

The volume of waste in Tank 241-SY-101 was first noted to increase in 1977 after the first double-shell slurry was put into the tank. This phenomenon was called slurry growth. After the last double-shell slurry campaign, the waste continued to grow and then dropped several inches during a gas release. This cyclic growth and subsequent drop has continued.

Figure 1 shows the cycles of the surface level of the tank during the past several years. Water and air lancing was used for a number of years in an attempt to control the gas releases in the tank. Lancing was stopped in 1989 when the surface level reached 423 in. This was greater than the 422-in. operating specification, which is in place to prevent overfilling the tank and overstressing it due to hydrostatic head.

When gas is released into the tank dome spaces, the pressure in the dome space increases. This is an indication that gas is being released. Early laboratory work to identify the cause of the slurry growth phenomena duplicated the gas release phenomenon and indicated that hydrogen is a major component of the slurry growth gas. Since early 1990, there has been an ongoing vapor sampling effort. In addition to hydrogen, subsequent work has identified nitrous oxide, nitrogen, and ammonia among the gases vented.

Table 1. Tank 241-SY-101 Contents.

Tank fill chronology	Gallons	Substance	Inches
April 1977	274,000	Double-shell slurry[a]	100
November 1977	365,000	Complexed concentrate[b]	133
June 1978	131,000	241-SX-106 Complexed concentrate	48
August 1978	60,000	111-U Complexed concentrate	22
November 1980	230,000	Double-shell slurry	84
September 1984 to May 1988	8,000	Water	3
Total	1,068,000		390

[a]Double-shell slurry is a concentrated waste produced by the evaporator. It is high in hydroxide, nitrate, and aluminate concentration.

[b]Complexed concentrate is an evaporator product similar to double-shell slurry (though not as concentrated). It also contains significant organic complexant concentrations.

Table 2. Tank 241-SY-101 Total Composition.

Component	Concentration
NaOH	3.22 M
NaAlO$_2$	1.90 M
NaNO$_2$	3.28 M
NaNO$_3$	4.23 M
Na$_2$CO$_3$	.62 M
Na$_2$SO$_4$	.12 M
Na$_3$PO$_4$	.19 M
Pu	713 (g)
Sr	2.187 x 11^{11} (μCi)
Cs	3.10 x 10^{12} (μCi)
TOC	26.24 (g/L)
H$_2$O	594,600 (gal)

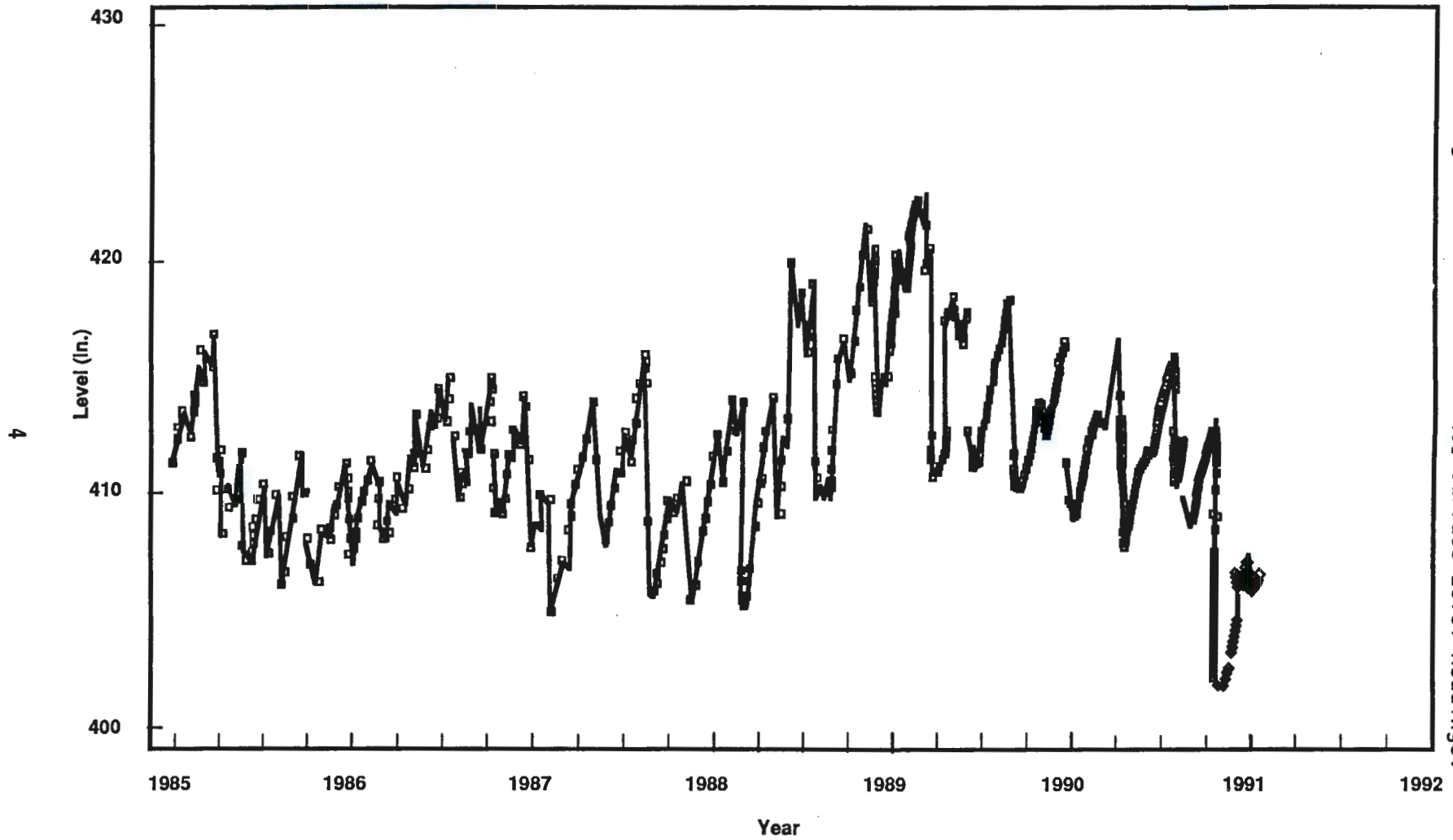NOTE: The concentrations are based on a present average tank height of 408 in.

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Figure 1. Tank 241-SY-101 Surface Level Readings.

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3.0 MONITORING OF TANK 241-SY-101

Semiquantitative identification of the species and amounts of the gases that are released from Tank 241-SY-101 has occurred through the evaluation of data obtained from (1) surface level measurements, (2) tank pressure, (3) flow rate of the ventilation system, and (4) measurement of the gas composition. In addition, significant insight into the venting process has been gained from interpretation of the temperature changes in profiles in the tank during gas buildup and release. The instrumentation used to monitor and characterize the tank is briefly described in the following paragraphs.

3.1 SURFACE LEVEL MEASUREMENTS

The original purpose of measuring the surface level in the tank was to monitor for leakage of waste tank contents and to ascertain when the tank was filled to the upper limit. Leakage would be indicated by a drop in surface level. In Tank 241-SY-101, an increase in the surface level indicated a "growth" of the slurry caused by entrapment of generated gases.

Three devices measure surface level in the tank--two conductivity probes and a radar gauge. The automatic conductivity probe is located at riser 1C. The manual conductivity probe (manual tape) is located at riser 17A. The radar gauge, installed in May 1991, is located at riser 13A. The layout of the risers in the tank is shown in Figure 2.

Both the automatic conductivity probe and the manual tape work on the same principle, described here in a simplified manner. One electrical contact point is made at the probe, the other at the tank wall. A low energy circuit is closed when the probe contacts the conductive surface of the waste. The level of the surface is determined by the amount of cable used to lower the probe to the level where the electrical contact is made. The automatic conductivity probe rises to break contact with the waste surface. This rising and lowering of the probe occurs at a preset interval as defined by the Computer Automated Surveillance System analysts. For normal operation, the cycle is repeated every 1.5 min; for enhanced operation (e.g., while obtaining more concentrated information on surface behavior during a vent episode), the cycle is repeated every minute. The Computer Automated Surveillance System has the capability of checking the automatic conductivity probe for its measurement either at the preset interval or upon request. The automatic conductivity probe can also be operated in a manual mode in the field.

The manual tape plummet is lowered into the tank until electrical contact is made with the surface of the waste crust. The reading is recorded on operations log sheets. Both the automatic conductivity probe and manual tape measurements are required daily. Generally, if the automatic conductivity probe is out of service, the frequency of manual tape readings is increased.

Several nonintrusive (noncontact) methods to determine the surface level have been considered as supplements to or replacements for the automatic conductivity probe and manual tape. A radar gauge was installed on the tank

Tank 241-SY-101 Plan View

Transmitter Box 101-6	20C
Annulus Inspection	18F
Gas Sampling Probe	17B
Annulus Inspection	10B
Annulus Inspection	18E
Spare	22A
Annulus Air Inlet	8B
Sludge Weight	23A
Temporary Lance	14A
Annulus Pressure Gauge	18D
Permanent Lance	1B
Transmitter Box 101-5	20B
Nonfunctional	24A
Annulus Inspection	9B
TV Camera	5A
Annulus Access	6A
Radar Gauge	13A
Supernate Addition	12A
Annulus Inspection	18C
Exhaust Port	7A
Manual Tape	17A
Annulus Exhaust Port	10A
Transmitter Box 101-4	20A
Annulus Inspection	18B
Spare	11A
Annulus Air Inlet	8A
Gas Sampling Probe	16A
Annulus Inspection	18A
Nonfunctional	25A
Annulus Inspection	9A

Pump Pit

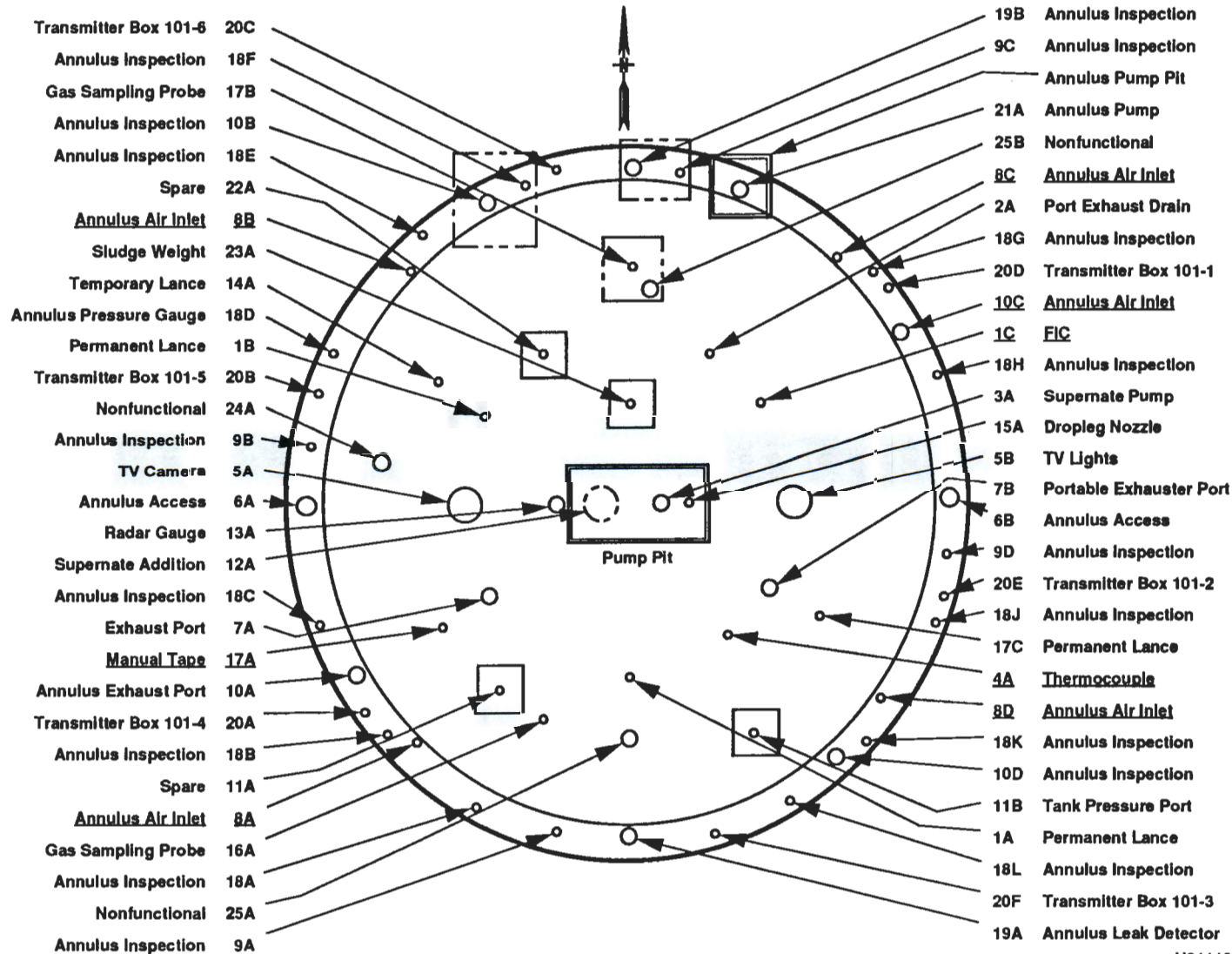|	
19B	Annulus Inspection
9C	Annulus Inspection
	Annulus Pump Pit
21A	Annulus Pump
25B	Nonfunctional
8C	Annulus Air Inlet
2A	Port Exhaust Drain
18G	Annulus Inspection
20D	Transmitter Box 101-1
10C	Annulus Air Inlet
1C	FIC
18H	Annulus Inspection
3A	Supernate Pump
15A	Dropleg Nozzle
5B	TV Lights
7B	Portable Exhauster Port
6B	Annulus Access
9D	Annulus Inspection
20E	Transmitter Box 101-2
18J	Annulus Inspection
17C	Permanent Lance
4A	Thermocouple
8D	Annulus Air Inlet
18K	Annulus Inspection
10D	Annulus Inspection
11B	Tank Pressure Port
1A	Permanent Lance
18L	Annulus Inspection
20F	Transmitter Box 101-3
19A	Annulus Leak Detector

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Figure 2. Tank 241-SY-101 Plan View.

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in May 1991. It is intrinsically safe and has a published accuracy of ±2 mm (±0.08 in.). It averages the level over an area of the crust surface and is not susceptible to errors due to icicle growth or pot-hole formation.

Readings from the radar gauge are shown on a digital LED display located in the 241-SY-271 (271-SY) instrument building. The radar gauge is still in a test mode, and readings are manually recorded on test data sheets by operators. When the testing phase is completed, collection of the radar gauge readings will be automated.

3.2 TANK PRESSURE

Two different pressure sensors are used on the tank. Pressure transmitter PT-101-1 monitors pressure at riser 11B (Figure 2). A pressure transducer converts pressure to a 4- to 20-milliamp (mA) current signal, corresponding to -4- to 6-in. water gauge (WG). This current signal provides input to a Chessell[1] strip chart recorder located in the 271-SY instrument building. Digital readout is available and is recorded on log sheets, if required. The 4- to 20-mA signal to the Chessell recorder is dropped across a 150-ohm resistor in series with a 100-ohm resistor, providing a 0.6- to 3-VDC output to the Wavetek[2] data logger.

The other differential pressure transmitter is located at riser 17B. The output signal is 4 to 20 mA, corresponding to -5 to +20 in. WG. The current loop signal is dropped across a 250-ohm resistor, yielding a 1- to 5-VDC input to the Hewlett-Packard[3] data logger.

3.3 VENTILATION FLOW RATE

The flow rate in the ventilation header (Figure 2) is measured by a flow rate meter. The device transmits a 4- to 20-mA current loop signal to the Chessell strip chart recorder. The signal corresponds to 0 to 1,200 ft^3/min of flow. This signal is dropped across a 150-ohm resistor in series with a 100-ohm resistor to provide an output signal to the Wavetek data logger of 0.6 to 3 VDC.

A second high-range flow transmitter is connected to a strip chart recorder. Its main purpose is to be able to monitor the flow during a gas venting, when the flow rate may approach or exceed 1,200 ft^3/min.

3.4 GAS COMPOSITION

Gas composition is determined by a number of methods. Some are used on a continual basis and some are used only when an event is thought to be imminent

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[1]Chessell is a trademark of Eurotherm International PLC.

[2]Wavetek is a trademark of Wavetek Corporation.

[3]Hewlett-Packard is a trademark of Hewlett-Packard Company.

with measurements continuing until sometime after the event. The devices and systems used are discussed briefly in the following paragraphs. Table 3 provides a summary of the gas monitoring equipment. Under the heading "Status," On-line indicates the system is on-line at all times; Event Only indicates the system is placed into service to monitor for the event.

The Teledyne[4] hydrogen monitor is located at the ventilation header and monitors for combustible gas in the ventilation system. The monitor determines hydrogen based on thermal conductivity. The monitor provides continuous output to a strip chart recorder and the Wavetek data logger.

Grab samples are taken at intervals determined by a Process Memo prepared prior to each event. They are analyzed in the 300 Area laboratory (mass spectrometer) and provide information about the gas composition. The samples are taken from a port in the ventilation line. The ventilation line port also feeds two gas chromatographs (one for hydrogen only, the second for other gases), the cryogenic sampler, and an ammonia system. These instruments are installed when an event is nearing.

The organic vapor monitor is installed at the SY tank farm stack by the Personal Protective Equipment approximately one week before the anticipated event. It is a nonspecific monitor that indicates ammonia. The readings appear to correlate well with Drager[5] tube sampling, which is used at the stack to indicate ammonia.

A Gas Monitoring System (GMS) was installed as a temporary system in April 1991. The gas is taken from a vapor space sampling tube located below riser 17B. The system instrumentation is housed in an instrument shelter on the SY tank farm, near the riser. The GMS is comprised of three main subsystems: (1) a molecular mass spectrometer which analyzes the gas for its components with atomic mass units between 2 and 100, (2) a hydrogen monitoring unit, and (3) a differential pressure transmitter.

The sample tubing runs from the riser location to the instrument shelter. A gas sample is drawn into the tubing and analyzed by the molecular mass spectrometer and the hydrogen monitor. The molecular mass spectrometer communicates with a personal computer located in the shelter. Data are then transmitted as an ASCII file over an RS-232 line to the Hewlett Packard (GMS) data logger. The hydrogen monitor provides a 4- to 20-mA current loop signal, which corresponds to 0% to 50%. The data are transmitted to the Hewlett Packard data logger.

Two other risers have three sampling tubes each installed for future use by an on-line GMS. These are not now in use but could be connected to provide a total of 10 gas monitoring locations in the tank (the ventilation header and 3 risers with three different levels in the dome space each). The plans for an additional on-line GMS are currently under development.

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[4]Teledyne is a trademark of Teledyne, Inc.

[5]Drager is a trademark of Dragerwerk AG Lubeck.

Table 3. Tank 241-SY-101 Gas Monitoring and Analysis.

Instrument	Location	Cycle time (event cycle time shown in brackets)	Gas components analyzed	Status
Gas monitoring system mass spectrometer	Riser 17B, near crust probe	5 min	N_2, O_2, H_2O, CO_2, N_2O, Ar, H_2, other gases	On-line
Gas monitoring system hydrogen monitor	Riser 17B, near crust probe	5 min, normal rate 10 s, fast rate [fast rate starts on increased pressure and/or hydrogen]	H_2	On-line
Teledyne hydrogen monitor	Vent header[1]	10 s, 1 min, or 10 min [set to 10 s in anticipation of the event]	H_2	On-line
Grab samples (off-line gas analysis)	Vent header[1]	[Sample every 10 min until hydrogen level is less than 1%; then sample every half hour for minimum 2 h; then sample every hour until termination requested]	N_2, O_2, CO_2, N_2O, Ar, H_2, He, CO, CH_4, NO_x	Event only
Ammonia system	Vent header[1]	[8 h (4 sets of 2 h each); auto start on -1 in. WG.]	NH_3	Event only
Cryogenic sampler	Vent header[1]	[4 h; auto start on -1 in. WG]	Organics, NH_3	Event only
Gas chromatographs (2)	Vent header[1]	[4 min cycle time. During and after event: continuous until hydrogen level is less than 1%; then sample every half hour for minimum of 2 h; then sample every hour until termination requested]	1 - H_2 specific 1 - Other gases (N_2, O_2, CO_2, N_2O, Ar, H_2, He, CO, CH_4, NO_x)	Event only
Organic vapor monitor	Stack, tank farm	[Install approximately 1 week before event; cycle time set to 1 min]	NH_3, organics	Event only

[1]The vent header gas sample port location is upstream of the psychometric port.

3.5 TEMPERATURE MEASUREMENTS

The temperature of the waste is obtained from a single thermocouple (TC) tree located at riser 4A. Eighteen Type J TCs are bonded pipe that is located in a 4-in. riser. Thermocouple 1 is the lowest TC in the tank, with higher numbered TCs higher in the tank. Thermocouple 17 is near the surface of the waste, and TC 18 is in the tank dome space above the waste. Table 4 provides the height of the TCs in the tank. Photographs taken in the tank show that the TC tree is slightly bent, so the heights given are not necessarily precise.

From the TC tree in the tank, TC wire is run through two junction boxes to an 18-position selector switch (SS-101-1) located in the 271-SY instrument building. The TCs are read manually using a hand-held digital TC reading device. These readings are recorded on log sheets daily, once a shift, or hourly, as directed by Process Memo. They have traditionally provided a record of the daily temperatures at the various heights in the tank. A parallel connection has been made from the TC wires to a Wavetek data logger, also located in the 271-SY instrument building. Prior to a gas release event, the recording interval is set to 10 s.

Table 4. Tank 241-SY-101 Thermocouple Numbers
and Locations.

Thermocouple number	Instrument number	Nominal height from tank bottom (in.)
T/C 1	TE-101-37	4
T/C 2	TE-101-38	28
T/C 3	TE-101-39	52
T/C 4	TE-101-40	76
T/C 5	TE-101-41	100
T/C 6	TE-101-42	124
T/C 7	TE-101-43	148
T/C 8	TE-101-44	172
T/C 9	TE-101-45	196
T/C 10	TE-101-46	220
T/C 11	TE-101-47	244
T/C 12	TE-101-48	268
T/C 13	TE-101-49	292
T/C 14	TE-101-50	316
T/C 15	TE-101-51	340
T/C 16	TE-101-52	364
T/C 17	TE-101-53	412
T/C 18	TE-101-54	460

In addition to the TCs in the tank space, a TC and temperature transmitter are located in the ventilation header space. The ventilation temperature data and relative humidity are logged to a Hewlett-Packard data logger located in the GMS shelter.

4.0 SUMMARY OF GAS RELEASE EVENTS

In the spring of 1990, an increased emphasis was placed on the characterization of the gas releases from Tank 241-SY-101. In the past 2 years, these episodic releases have occurred about every 100 days. Table 5 provides a summary of the events of 1990 and 1991.

Table 5. Periodic Release of Gases.

Event date	Number of days since last event	Change in surface level, in.	Peak pressure, in. (WG)	Peak H_2 conc., %
January 1990	109	-7.7	-	-
April 19, 1990	110	-8.3	+0.1	3.5
August 5, 1990	109	-5.2	-1.96	1.2
October 24, 1990	80	-10.3	+2.3	4.7
February 13, 1991	110	-5.0	-2.0	0.04
May 16, 1991	82	-7.2	+0.25	0.5
August 1991	--	≤5	-2.83	0.56

It is not the intent of this report to provide a detailed description of each event; rather, selected observations will be presented. Detailed reports are issued for each gas release event.

4.1 GAS RELEASE EVENT OF APRIL 1990

On April 19, 1990, Tank 241-SY-101 started to release gas, and the majority of the release occurred in a 6- to 8-h period. This event released sufficient gas to briefly pressurize the tank dome space to +0.1 in. WG and caused the hydrogen concentration to peak at about 3.5 vol% in the exhaust header. This is shown in Figure 3. The total surface level drop was 8.3 in., but the lowest level did not occur until 11 days after the event. Several instruments were employed to evaluate the concentration of hydrogen during the event. From those listed in Table 3, the April 1990 event utilized the Teledyne monitor, a gas chromatograph, and a grab sample, which were sent to a laboratory mass spectrometer. Figure 4 shows that good agreement was obtained between the three systems. Data from the mass spectrometer evaluations showed that nitrous oxide was also released during the event. An estimation technique for the gas composition showed that it was 30 to 33 mol% hydrogen and 20 to 25 mol% N_2O (Allemann 1991). A detailed evaluation of the April 19, 1990 event is given in Burke et al. (1991).

4.2 GAS RELEASE EVENT OF AUGUST 1990

Unlike the April 1990 event, the August 1990 event was very mild. Both the surface level and pressure response indicated a much slower release of gas. The total surface drop was 5.2 in., and the peak hydrogen concentration in the exhaust header was about 1.2%. As with the April 1990 event, the various instruments provided good agreement on the hydrogen release, which is
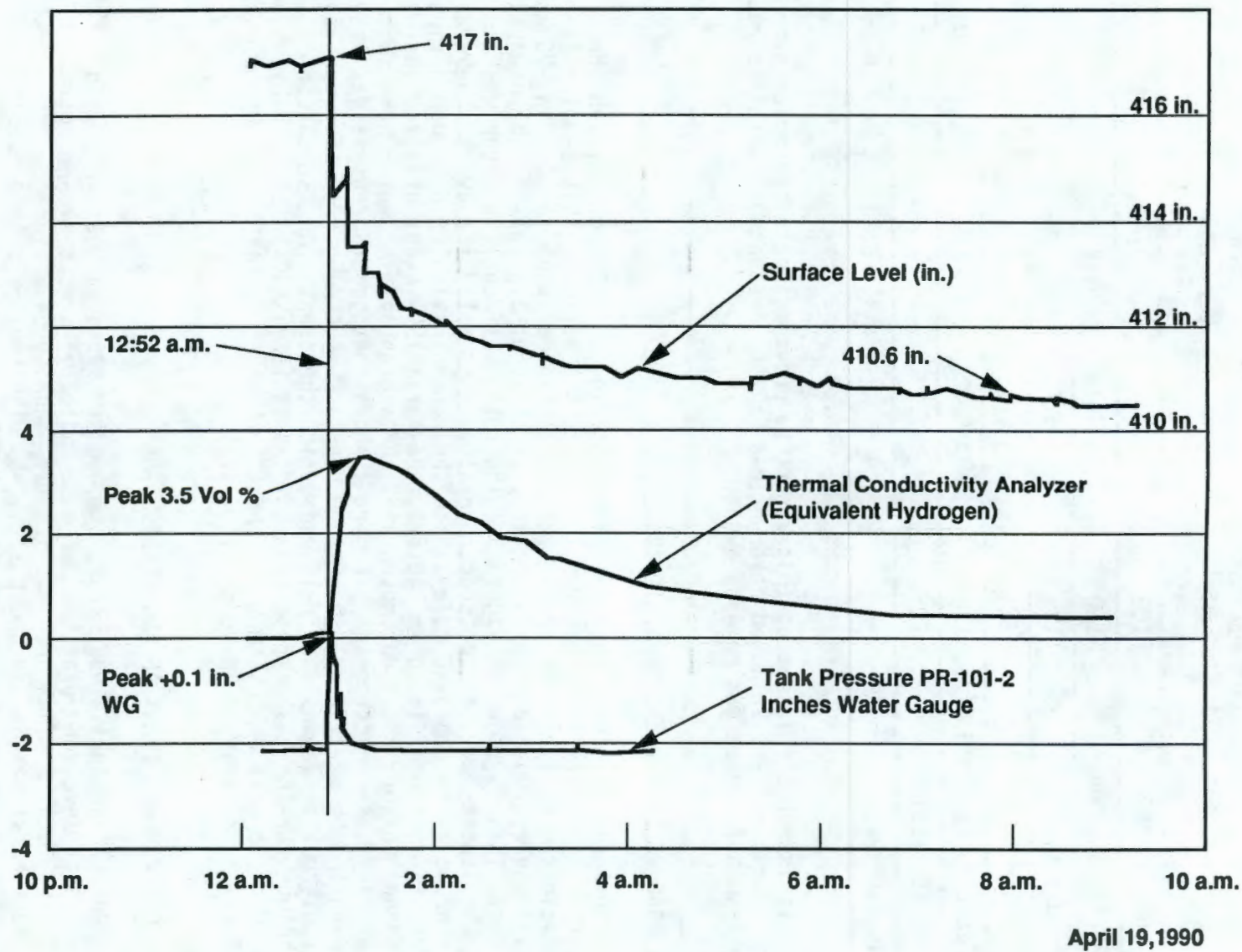
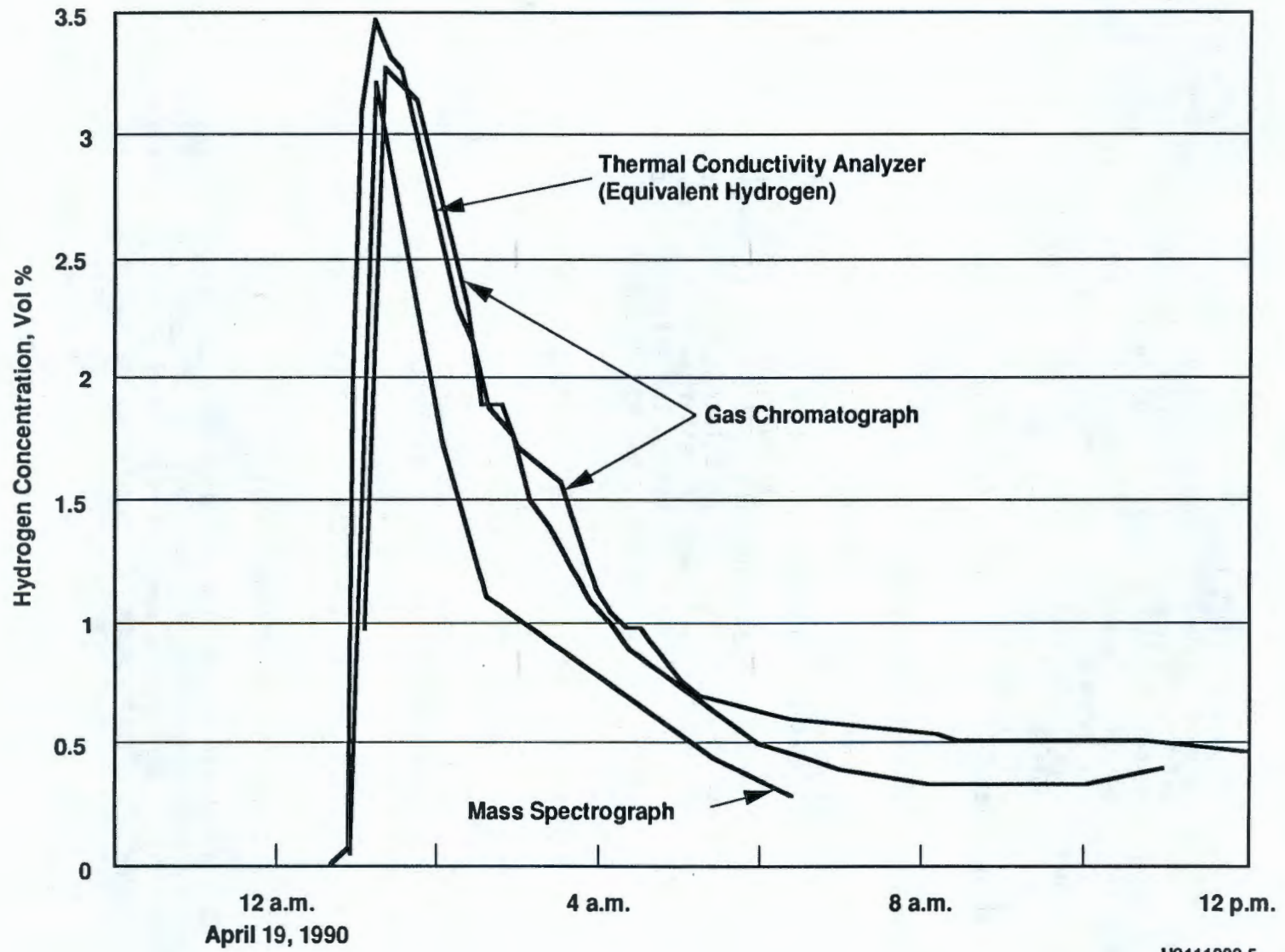Figure 3. Tank 241-SY-101 April 19, 1990 Event 12-h Plot.

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Figure 4. Tank 241-SY-101 April 19, 1990 Event--Exhaust Gas Hydrogen Concentration.

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shown in Figure 5. Grab samples of the gas were sent to the Idaho National Engineering Laboratory for analysis with their precision mass spectrometer. The mean composition from these analyses was 40 mol% hydrogen (±1.4), 32.9 mol% nitrous oxide (±1.2), and 28 mol% nitrogen (±2.1).

Figure 6 shows the temperature profiles of the tank both before and after the event. Before the event, the temperature profile exhibited a pronounced bulge in the lower portion, a nearly isothermal region in the upper portion, and a steep gradient at the top surface. During a gas release event, it has been postulated that the waste in the lower region moves to the upper region because of excess buoyancy. The temperature profile shows a decrease in temperature in the "bulge" in the lower part and an increase in temperature just below the waste surface. After the gas has been released, the temperature profile gradually reverts to the pre-event condition. A detailed evaluation of this event is given by Carothers et al. (1989).

4.3 GAS RELEASE EVENT OF OCTOBER 1990

One of the improvements added to the instrumentation systems before the October 1990 event was the capability to record the temperature at 10-s intervals. Just before a high-pressure alarm signaled a release in the morning of October 24, 1990, the temperature profile underwent a rapid reversal. Temperature records showed that the upward movement of the hotter material started about 10 s before the colder material moved downward. The entire tank appeared to "roll over" in less than 90 s. This is illustrated in Figures 7, 8, and 9. Figures 7 and 8 show the entire profile, while Figure 9 shows data for only two thermocouples, one at the bottom (#4) and one at the top (#16).

The October 24, 1990 event has been the "largest" event ever recorded for Tank 241-SY-101 in that the event produced the largest amount of hydrogen, the largest increase in pressure, and one of the largest drops in surface level. Figure 10 provides a summary of the pertinent data. Again, good agreement on the amount of hydrogen released was found for the three measurement methods shown in Figure 11. A comparison of the hydrogen release for the April, August, and October 1990 releases is given in Figure 12.

Barker (1991) provides the detailed analysis of the October 1990 event.

4.4 GAS RELEASE EVENT OF FEBRUARY 1991

This event was rather mild, in that there was little increase in either the tank pressure or hydrogen concentration. A total drop of 5 in. was recorded over a period of 9 days. No data were obtained on gas composition. The temperature profile change for this event is provided in Figure 13. Note that only a partial "rollover" occurred; this was quite similar to the August 1990 event (Figure 6). A report for this event is being prepared and is scheduled for release in November 1991.

Figure 5. Tank 241-SY-101 August 5, 1990 Event--Exhaust Gas Hydrogen Concentration.
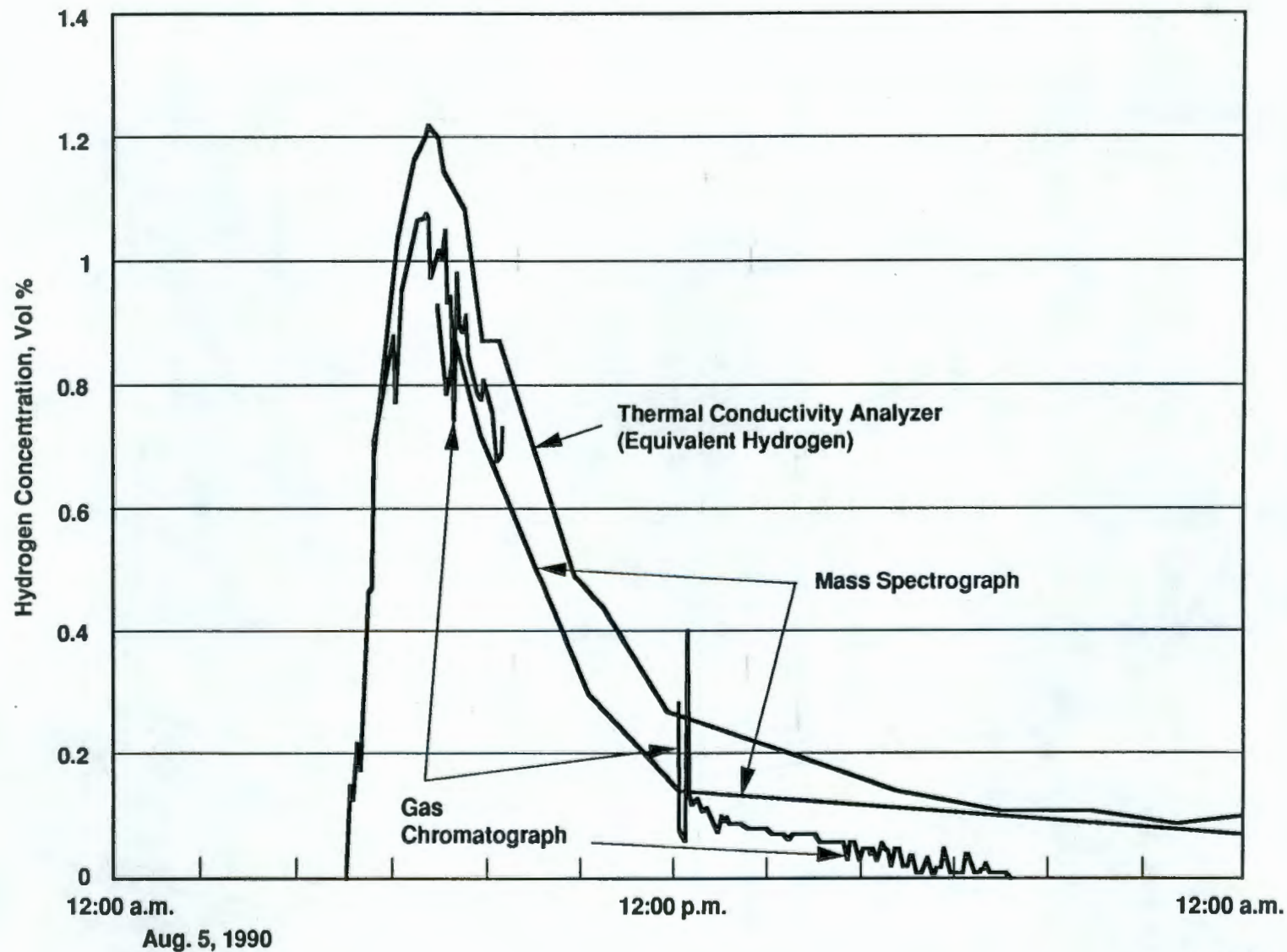
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Figure 6. Tank 241-SY-101 August 5, 1990 Event--Temperature Profiles.

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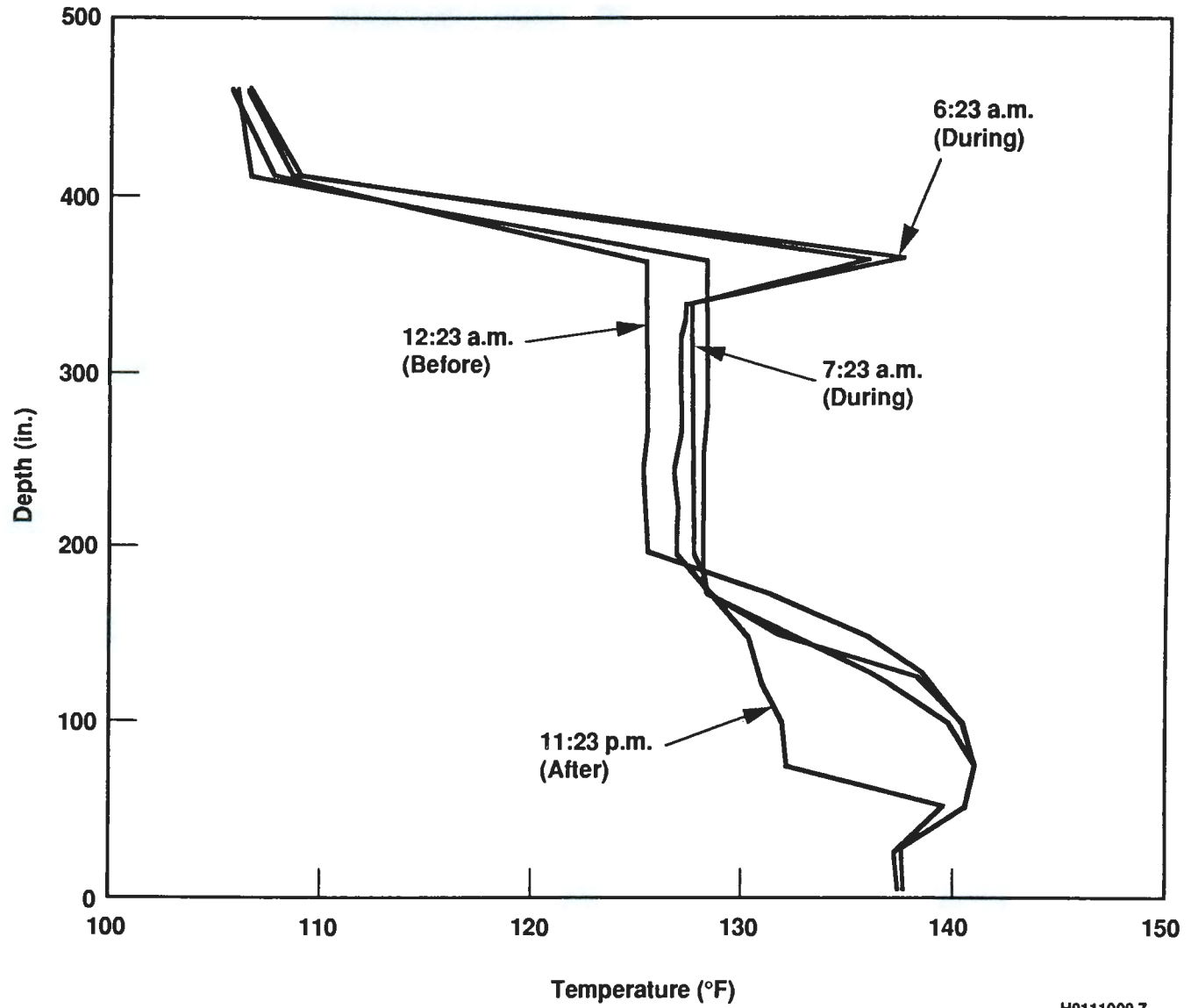
Figure 7. Tank 241-SY-101--October 24, 1990.
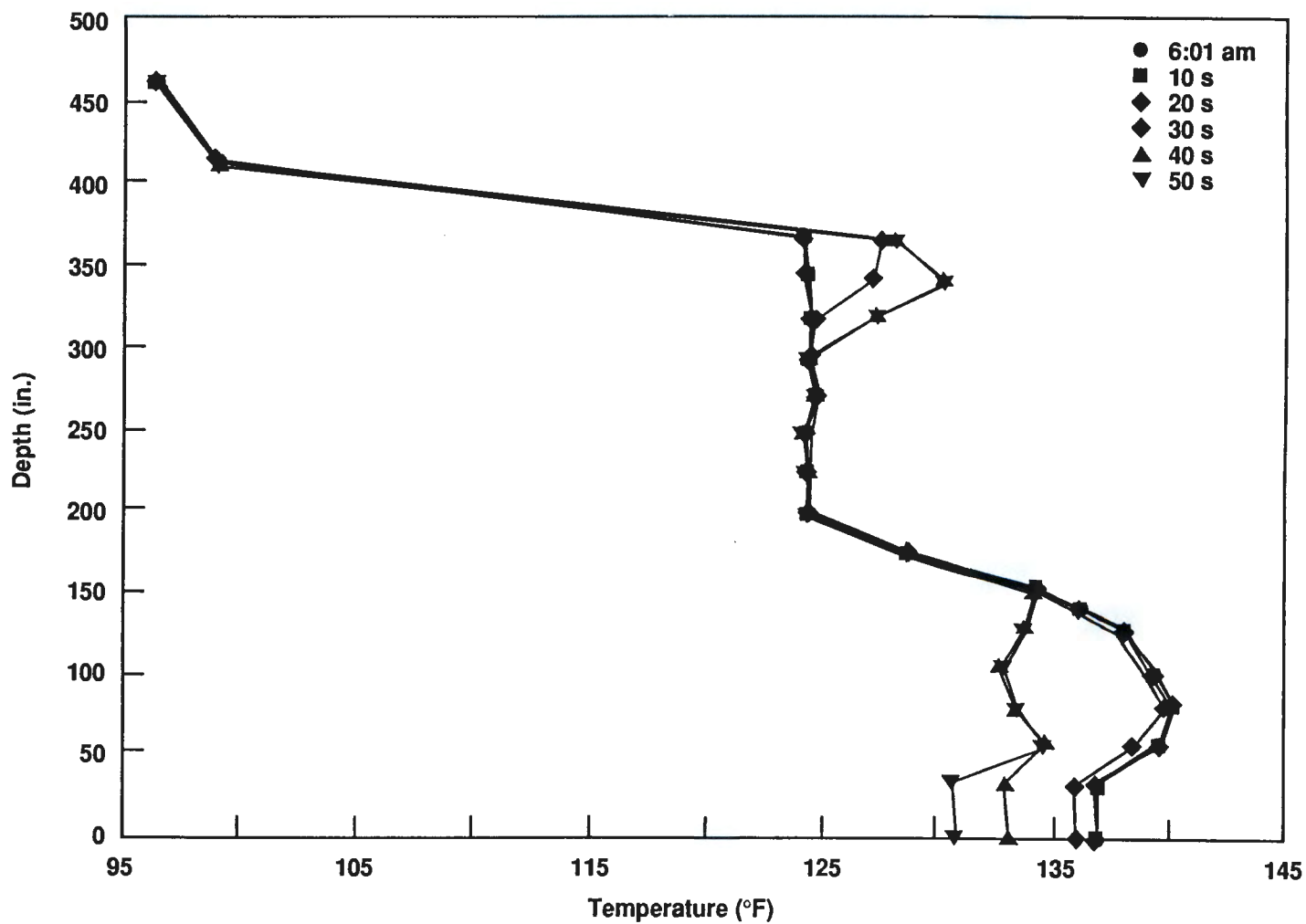
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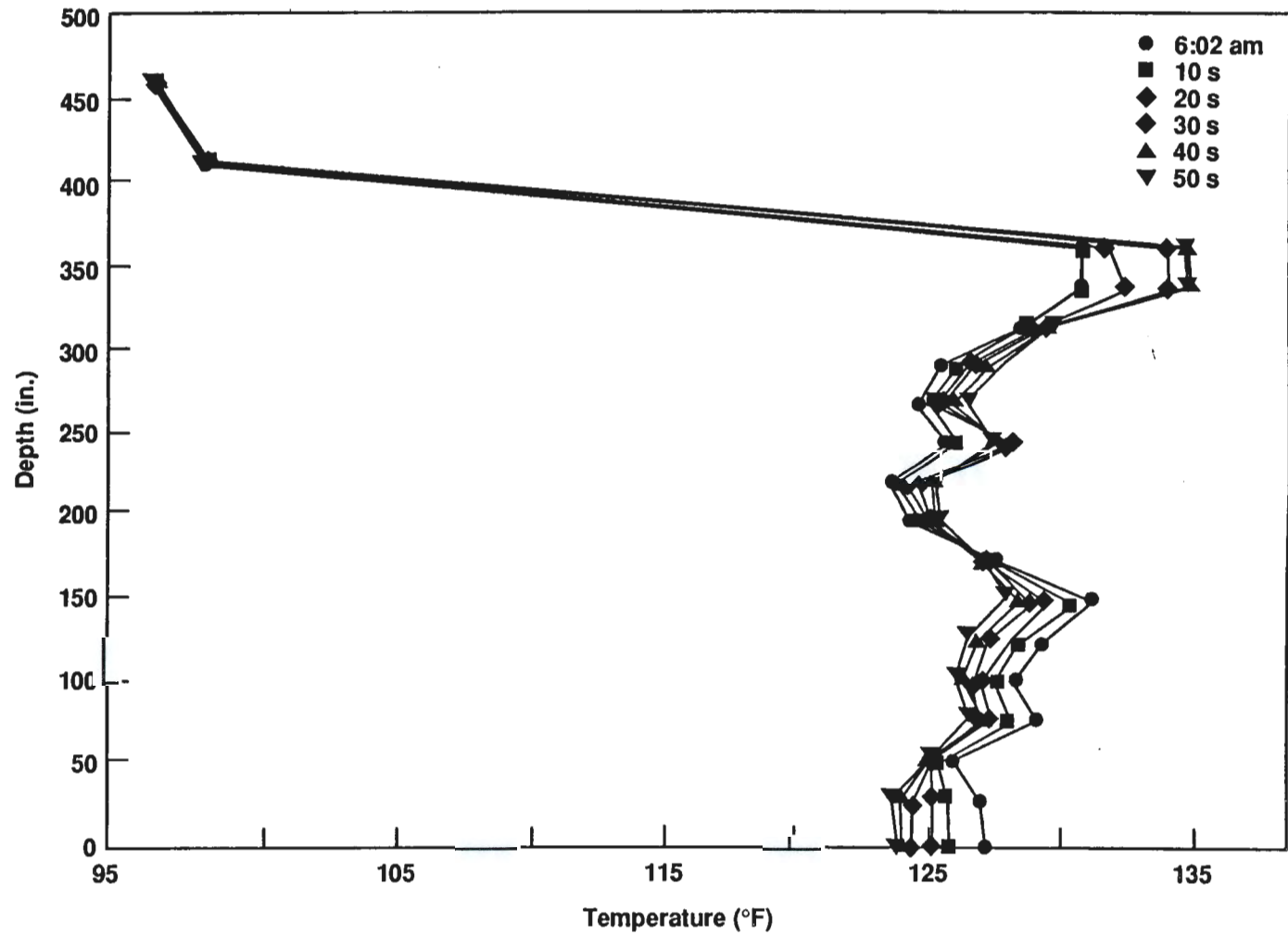
Figure 8. Tank 241-SY-101--October 24, 1990.

29101012.7a
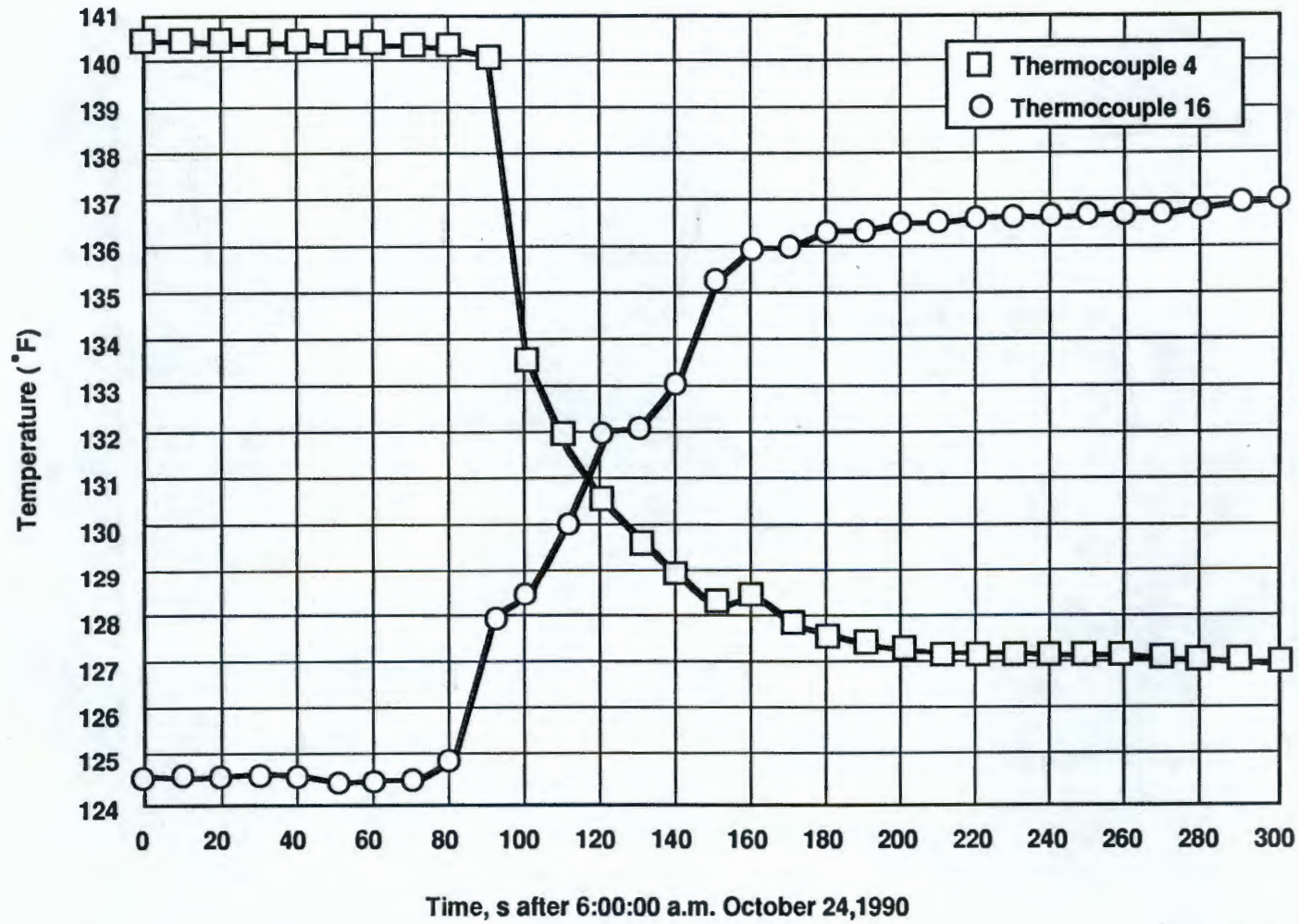
Figure 9. Temperature Versus Time Around Gas Release Event for 300 s.

Time, s after 6:00:00 a.m. October 24,1990

79106024.2a

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19
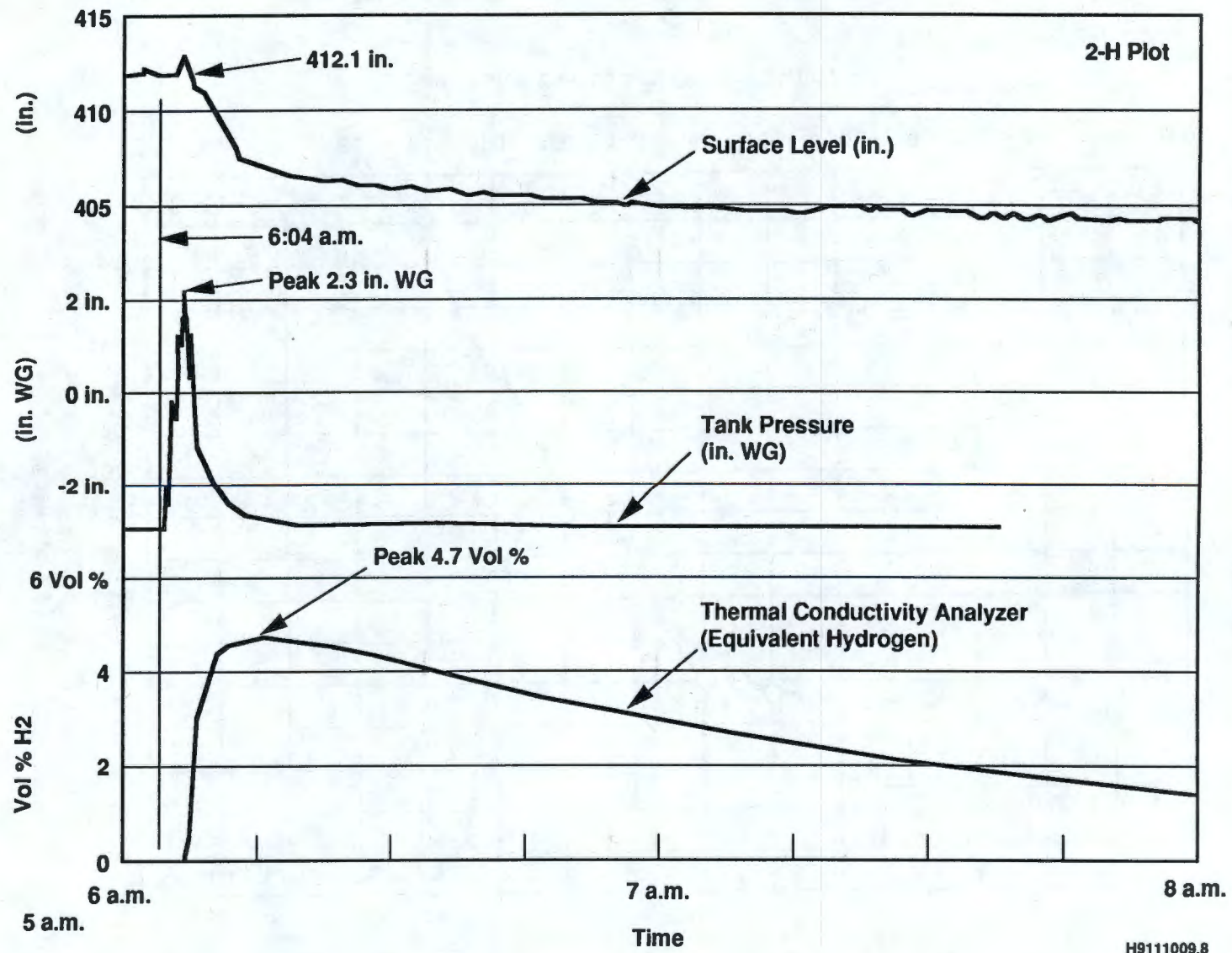
Figure 10. Tank 241-SY-101 October 24, 1990 Event.

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H9111009.8

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21

Figure 11. Tank 241-SY-101 Gas Venting--Hydrogen Concentration Comparisons.

Gas Chromatograph

**Teledyne
(equivalent hydrogen)**

Mass Spectrograph

Hydrogen (vol%)

5
4
3
2
1
0

5 a.m.   8 a.m.   12 p.m.   5 p.m.

Figure 3-4

79106024.4

Figure 12. Tank 241-SY-101 Gas Venting--Hydrogen Concentration Comparisons.

Figure 13. Thermocouple Temperature Comparison Before, During, and After Event.

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23
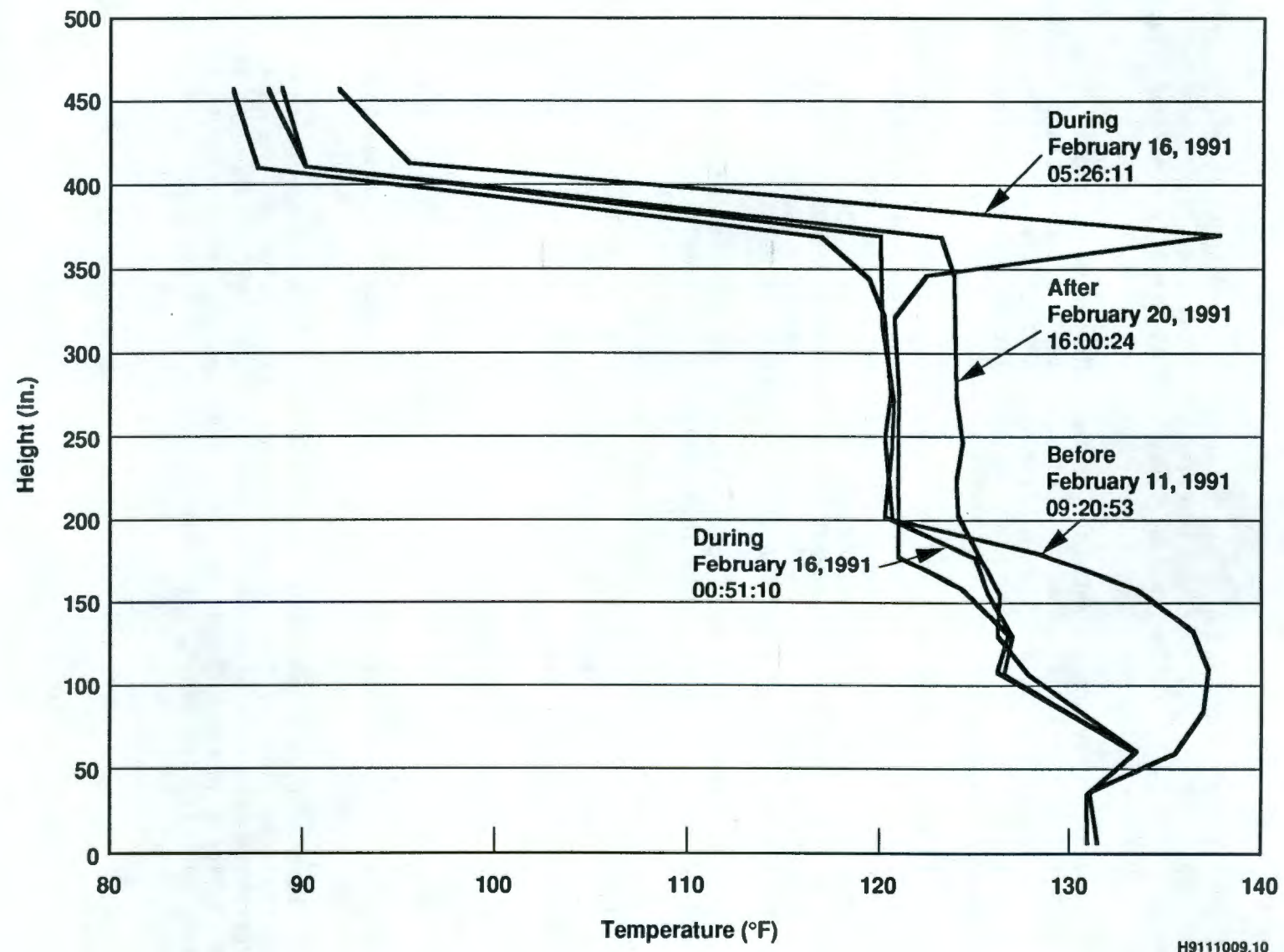
H9111009.10

4.5 GAS RELEASE EVENT OF MAY 1991

Before this event, the on-line mass spectrometer and a hydrogen-specific monitor were set up to sample a probe that had been inserted into the tank dome space at riser 17B.

The tank pressure and hydrogen behavior in the exhaust header for this event are shown in Figure 14. This event did produce a slight positive pressure of 0.25 in. WG in the dome space, but it was at a positive value for less than 20 s.

Figure 15 provides a comparison of the hydrogen measurements from the tank dome space and in the exhaust header. Note that the Whittaker[6] unit was used for the dome space and the Teledyne unit sampler for exhaust header. For each location there is good agreement between the hydrogen-specific monitor and the results from a mass spectrometer.

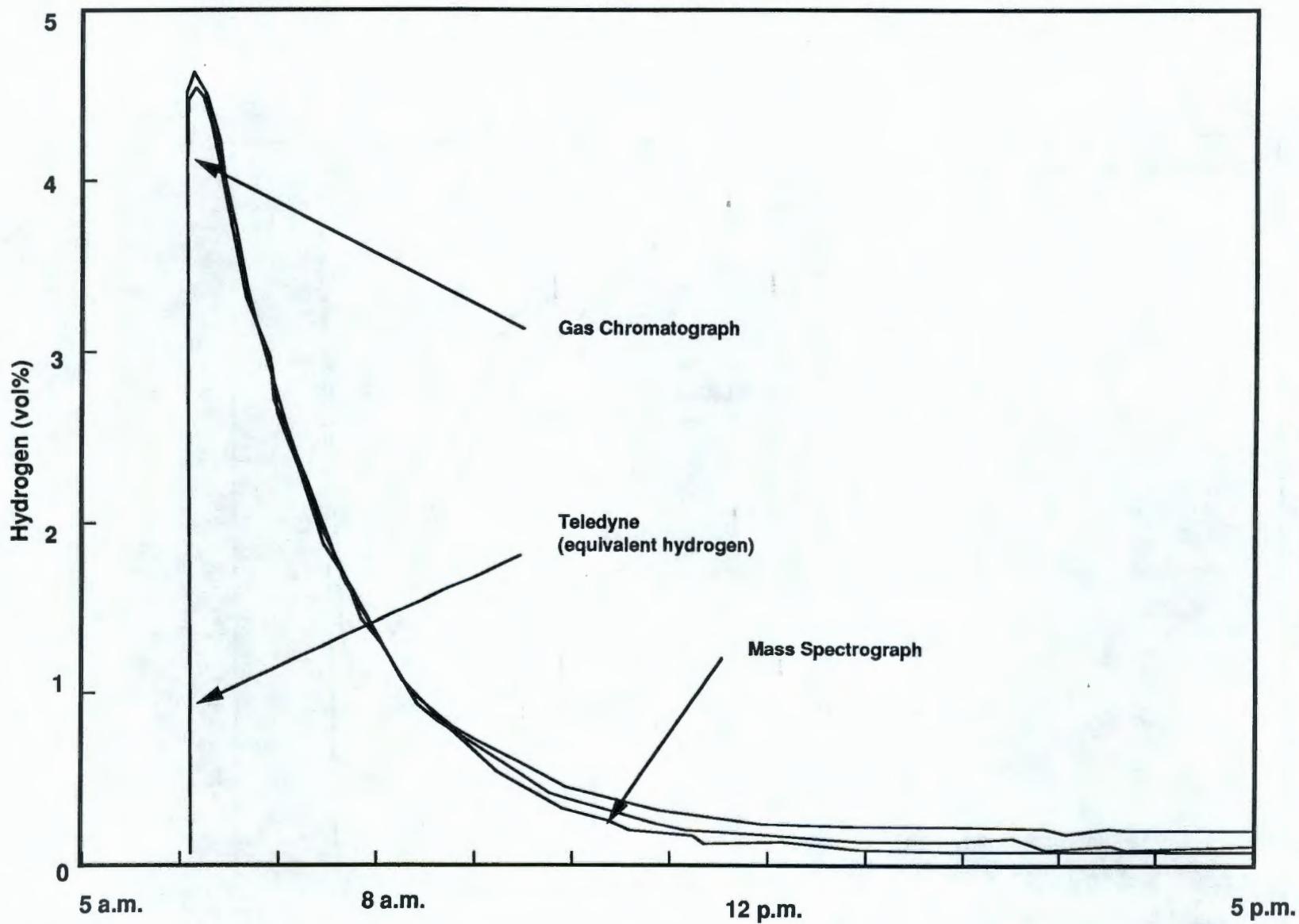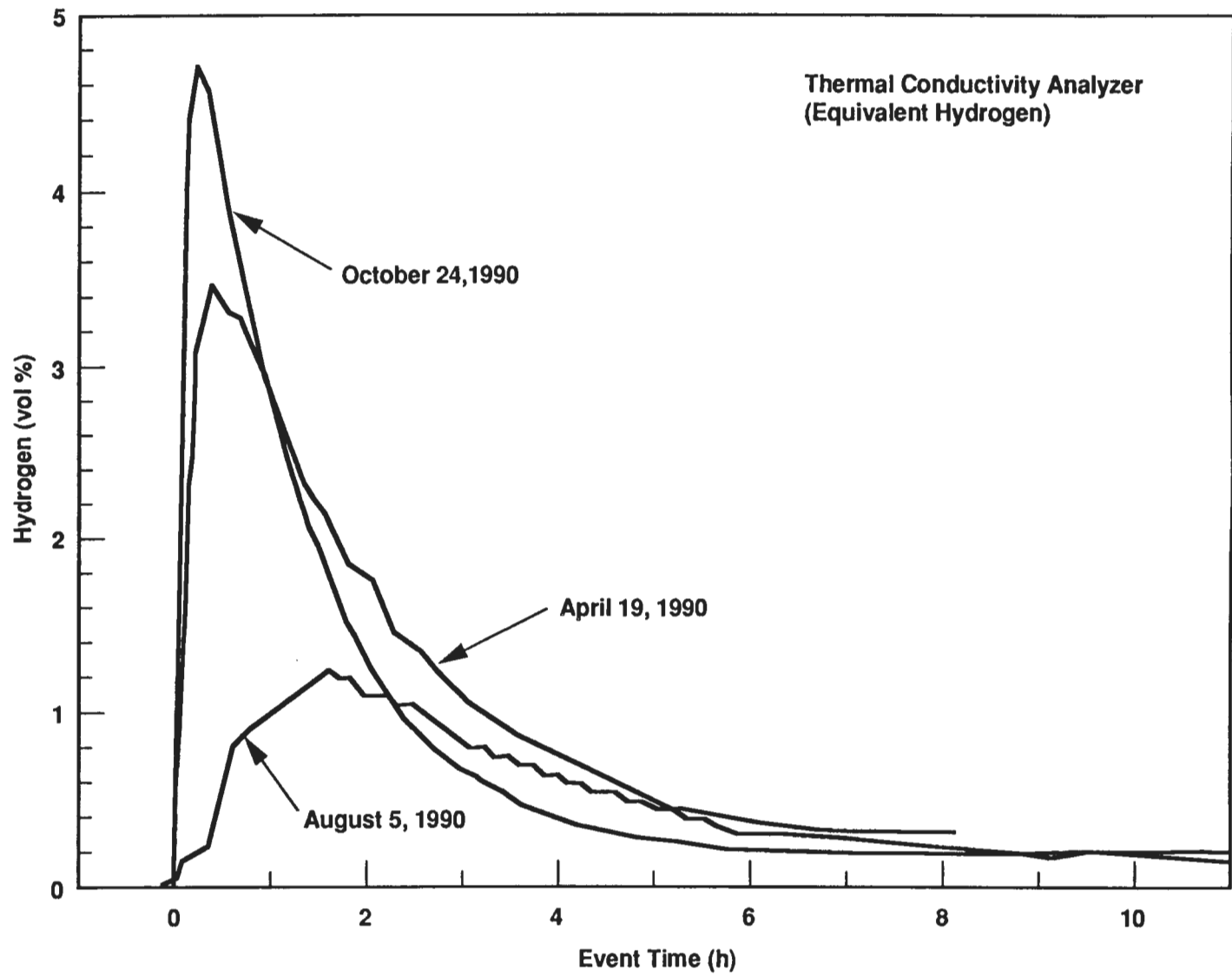While these methods do agree well with the concentration of hydrogen in the vapor space, the hydrogen monitors cannot estimate the gas composition. The gas composition is estimated by the mass spectrometer samples. Two different mass spectrometer instruments are being used. Grab samples were taken and sent to Pacific Northwest Laboratory for high-resolution mass spectrometer analysis. The on-line mass spectrometer measures gases at near real time from the sample port about 18 in. above the waste.

Based on the on-line mass spectrometer analyses, the composition of vented gas was estimated. To do this, only the gas samples that had over 1% hydrogen were considered to ensure that the vent gas would be in larger quantities and the analysis would be more accurate. Because of the greater dilution in the ventilation system, none of the grab samples indicated greater than 1% hydrogen. Therefore, these samples are too dilute to yield meaningful gas compositions, and the on-line mass spectrometer was used for the May 1991 event gas composition estimates.

The gas analyzed by the on-line mass spectrometer is a combination of ventilation air mixed with the gas released by the waste. The released gas tends to be a small portion of the total. To estimate this gas, the argon is used as a tie element so that an amount of air proportional to the argon is subtracted from the measured gas to get the estimated gas composition released from the waste.

The amount of argon in the samples varied, which influenced the final results. For example, the air measurements taken by the on-line mass spectrometer had an average argon concentration of 0.92%. There is about a 10% variation in the argon value. When the argon is used to adjust larger values such as nitrogen, a small variation makes a large difference in the answer.

When air was subtracted out of the measured composition using argon as a tie element, the oxygen varied around zero. There were approximately the same number of negative values as positive values. This indicated that oxygen

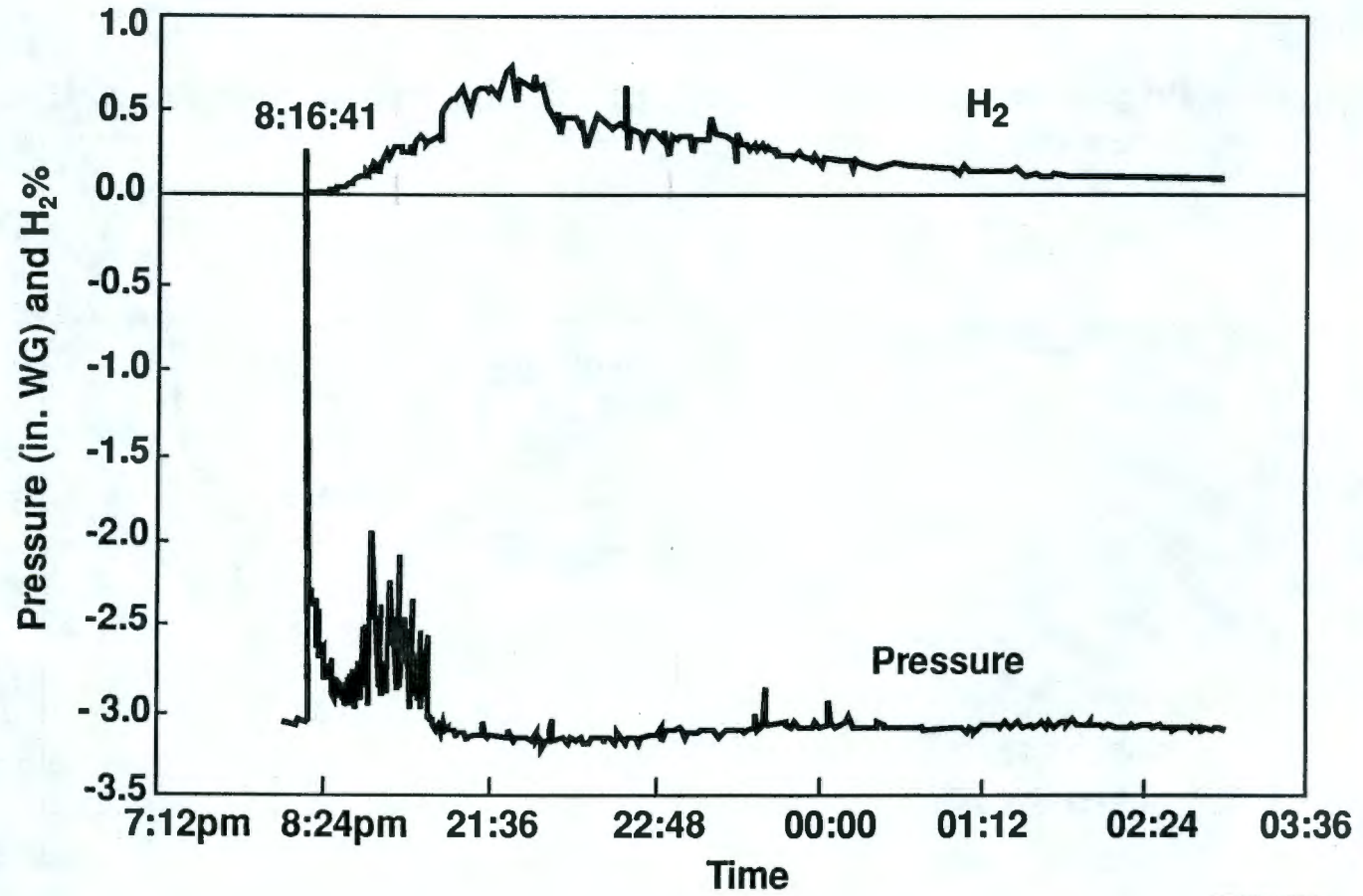---

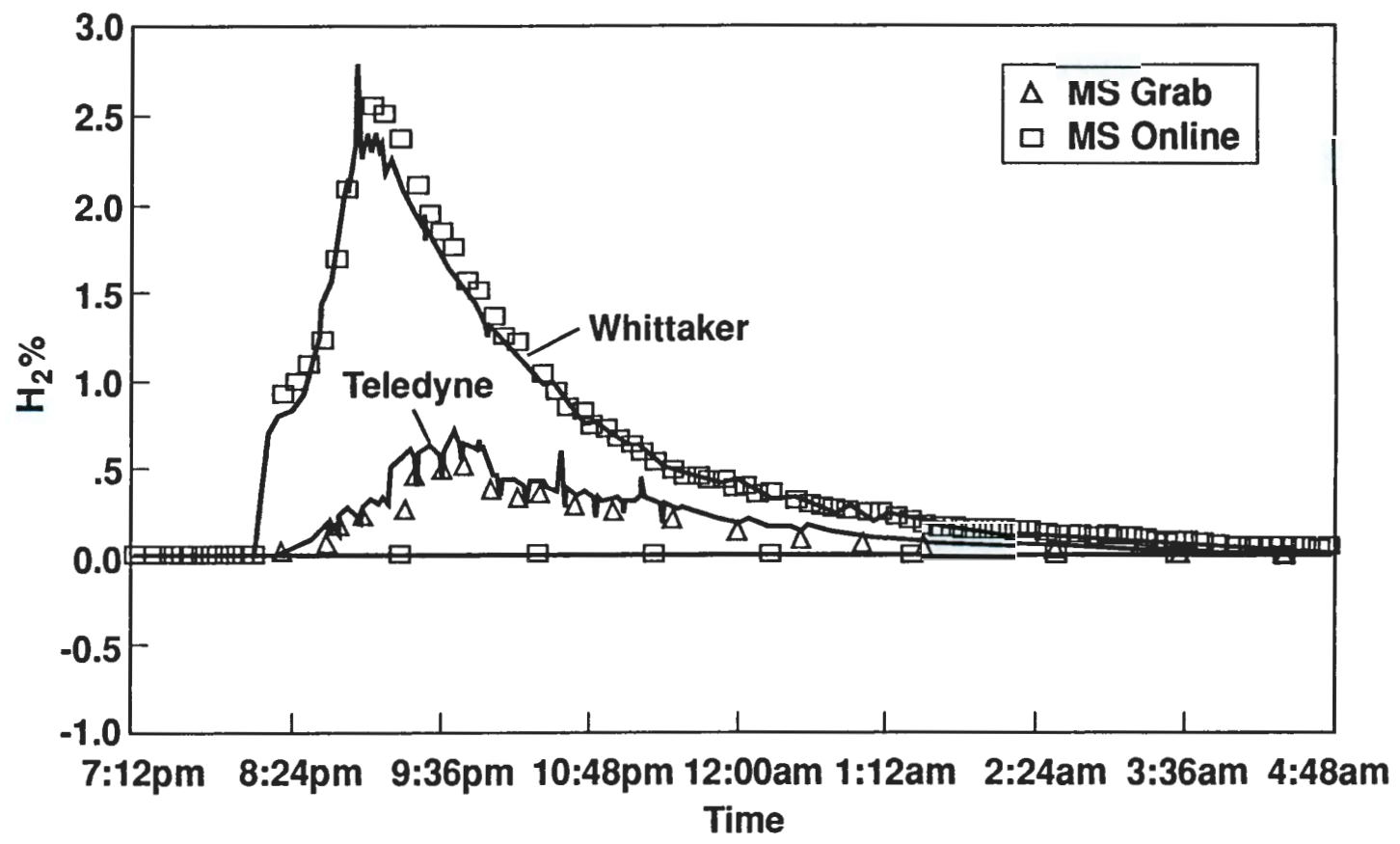[6]Whittaker is a trademark of Whittaker Electronic Resources.

Figure 14. Pressure and Hydrogen Profiles, May 1991 Gas Release Event.

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79108147.9e

Figure 15. Hydrogen Release Profile May 1991 Gas Release Event.

79108147.10e

probably is not part of the vent gas. The oxygen values were set to zero, and the resulting gas composition was normalized to 100%. The results are tabulated below.

Estimated gas composition	
H_2	15.4%
H_2O	17.7%
N_2	57.7%
N_2O	9.1%
CO_2	.1%

It should be pointed out that the water may not be measured accurately with the on-line mass spectrometer. The mass spectrometer is not kept at the same temperature as the tank head space so the water may condense. Also, the moisture may represent some water that was evaporated into the ventilation air when the air came in contact with the waste. Water certainly does play a large part in the composition of the gas.

One of the differences between the grab sample mass spectrometer analysis and the on-line mass spectrometer analysis was the nitrous oxide-to-hydrogen ratio. The N_2O/H_2 ratio for the grab sample has measured near 0.75 for several gas ventings. The on-line mass spectrometer indicates that this ratio would be closer to 0.6. Perhaps the problem is that part of the response to nitrous oxide is recorded in mass 45 instead of mass 44. This would make the reported response of nitrous oxide lower than actual value.

The gas composition determined by the on-line system is different than that from the gas sampler (Sections 4.2 and 4.8). The values reported here for the on-line mass spectrometer are still being reviewed and evaluated. There is ongoing work both at Westinghouse Hanford Company and Pacific Northwest Laboratory to try to improve the understanding of the released gases, and a full discussion will be provided in the evaluation report for the event.

4.6 GAS RELEASE EVENT OF AUGUST 1991

During the period of August 26 to 29, 1991, Tank 241-SY-101 exhibited some of the characteristics associated with a gas release event. This event appeared to be similar to the events in August 1990 and February 1991. There was a very small increase in tank pressure and hydrogen concentration. The temperature profile did not exhibit a full reversal.

The on-line mass spectrometer peaked at 0.28% hydrogen and the Whittaker unit recorded 0.38% H_2. An increase of 0.13% H_2 was noted by the Teledyne monitor on the exhaust header.

Video recordings on August 26 and 27 showed areas that "rolled over" together with numerous bubbles. Even though the television camera showed considerable surface movement of the waste, the TC data did not show the complete removal of the "temperature bulge" in the lower portion of the tank.

An additional piece of information from the mass spectrometer and the humidity monitor in the exhaust header showed significant increases in relative humidity on both August 26 and 27 (see Figure 17).

4.7 AMOUNT OF GAS RELEASED IN AN EVENT

Using the estimates of gas composition, the flow rate for the ventilation and the hydrogen release profiles (e.g., Figure 12), it is possible to estimate the total amount of gas released in the various events. The most recent set of analyses was given in Barker (1991). A summary of the calculations is given in Table 6.

The released gas volume can also be calculated from the change in the surface level of the tank. Assuming that the entire surface of the tank waste moves in a uniform manner during an event and that the gas behaves as an ideal gas, the volume of gas was calculated for two cases: (1) the specific gravity of the waste equals 2, and (2) the specific gravity equals 1.6. Table 7 presents the results. These values are in general agreement with those in Table 6.

4.8 BEST ESTIMATE OF GAS COMPOSITION

In Section 4.2, the composition of the gas, based solely on mass spectrometer data, was 40% H_2, 32% N_2O, and 28% N_2. Barker (1991) reported that the October 1990 data yielded a composition of 38% H_2, 32% N_2O, and 30% N_2. These two results are in good agreement, considering the difficulties in estimating the constituents in a diluted gas stream. These analyses do not account for the condensable gases (H_2O and NH_3). Barker (1991) showed that ammonia was detected during the October 1990 event, and most recently it was also detected in the May 1991 event. Figure 17 shows that water vapor also is present. In consideration of the fact that the trapped gases at the bottom of the waste are under about two atmospheres of pressure and that the total pressure is composed of the vapor pressure of the various gases, a calculation was made to determine the amount of minor constituents in the released gases. At this point in time, the best estimate for the gas composition is as follows:

Hydrogen	36%
Nitrogen	37%
Nitrous oxide	28.5%
Water	4%
Ammonia	4%
ΣCO_2, CH_4 CO	0.5%

Continued monitoring of the tank will help to improve the knowledge of the specific gases released in the events.

Figure 16. Tank 241-SY-101--Relative Humidity.
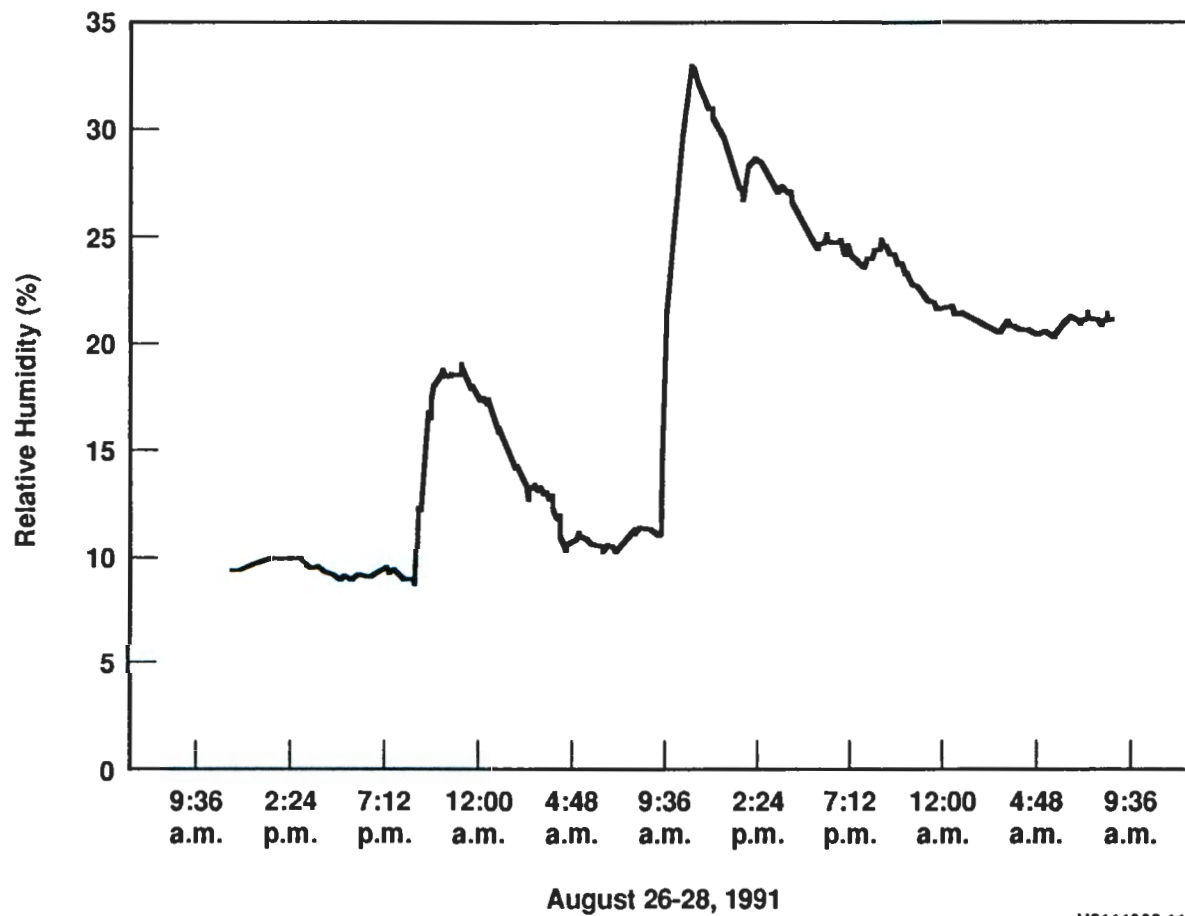
H9111009.11

Table 6. Comparison of Data from Three Gas Release Events.

Date	Crust level change (in.)	Pressure peak (in. WG)	H_2 concentration peak (mol%)	H_2 gas release[a] (ft^3)	Total gas release[a] (ft^3)	Steady-state ventilation flow rate (ft^3/min)
4/19/90	-9.3	+0.1	3.5	3,600	11,000 ±2,700	371
8/05/90	-5.2	-1.96	1.2	1,900	7,000[b] ±3,600	417
10/24/90	-10.2	+2.3	4.7	3,200	8,400	600

[a]Calculated values.
[b]Assumes 27 mol% hydrogen in evolved slurry-growth gas. At 40 mol% hydrogen, total gas amounts to 4,800 ±450 ft^3.

Table 7. Gas Volumes for Events.

Date	Drop (ft³)	Minimum (ft³)	Maximum (ft³)
April 1990	9.3	6,140	8,930
August 1990	5.2	3,430	4,990
October 1990	10	6,600	9,600
February 1991	5	3,300	4,800
May 1991	7.2	4,300	7,200
August 1991	5	3,000	5,000

5.0 SUMMARY OF STUDIES CONDUCTED TO DETERMINE THE MECHANISMS FOR GAS GENERATION

5.1 POSSIBLE MECHANISMS OF TANK BEHAVIOR

A number of hypotheses have been proposed to explain the mechanisms of gas generation, but more information from characterization, modeling, and laboratory simulation studies is needed before we can fully understand and plan to mitigate the tank hazards. Work is in progress at Westinghouse Hanford Company, Argonne National Laboratory, the Georgia Institute of Technology, and Pacific Northwest Laboratory to determine the exact mechanism of gas generation and release. Since the cause of the cycle is not yet known, cyclic hydrogen generation and release is an unreviewed safety question.

Based on analysis of the off-gas stream, a mixture of hydrogen, nitrous oxide, and nitrogen gas appears to form as the product of radiolysis and/or the chemical decomposition of the organic chemicals in Tank 241-SY-101. Insight into tank chemistry and the processes associated with gas generation requires that information be obtained by taking a full core sample of the contents of the tank. According to our current hypothesis, tank gases appear to be formed continuously in the whole tank, but appear to be formed and stored preferentially in the nonconvective sludge layer in the bottom portion of the tank. This storage phenomenon creates a supersaturated "solution" of gas in the tank. Unknown instabilities trigger a movement of the waste towards the top of the tank thereby releasing the stored gas.

The temperature profile change (Figure 5-7) gives insight to the mechanism that causes the periodic releases. There seems to be a chemical reaction, assisted by radiation effects that generate the gas. The gas-trapping mechanism appears to be due to hydraulic and physical methods.

Before a gas release, the bottom part of the tank shows a profile that has a maximum temperature near the middle of this region. This is a classic shape temperature profile for material with a volumetric heat source and in which the heat is dissipated by conduction. The indications are that this layer contains settled solids that do not move. The radioactive decay heats

this layer uniformly, but the heat can flow from both the bottom and top of the layer. Hence, those areas are cooler than the center of the layer.

Above this layer is a layer that has a very uniform temperature. This is an indication of a fluid convective heat transfer zone. Heat generated in this zone and transferred to it from below is the driving force to move the fluid by convection. The convection mixes the layer and keeps the temperature uniform.

After a gas release, the temperature profile is commonly uniform. This shows that the entire tank has been stirred up, indicating a "rollover" in the tank. Indeed, when the temperatures are studied more closely, it is common to see the hot material from the bottom rise to the top and lodge there for some time.

While other mechanisms have been proposed, this rollover has stood up under scrutiny and explains the observations. Figure 16 shows a schematic of what is believed to be happening.

The chemical reaction (involving the organics and assisted by the radiation) is producing gas throughout the tank. In the convective layer, the motion of the fluid brings the gas generated in that layer up to the surface where it can be released. This does not allow the gas to accumulate in the fluid layer. However, in the lower layer, the waste does not move. Most of the gas formed in this layer is retained.

This layer becomes less dense due to the accumulated gas. The temperature rises, which does several things. The warmer temperature causes the accumulated gas to expand, further decreasing the density. The increased temperature decreases the viscosity of the material. Some of the solid material redissolves in the warmer temperature. The chemical reaction rate may also increase.

Finally, the lower level reaches a critical density and becomes buoyant. This causes instability, and the lower region rolls over to the top. When this happens, the hydrostatic head decreases, the pressure on the accumulated gas drops, and the bubbles expand. This further increases the buoyancy. The gas releases when it gets to the surface.

Eventually, enough of the accumulated gas is released so that the solids can settle out. The nonconductive layer forms once more on the bottom and the cycle starts over again.

The current thought is that the crust is not a barrier to gas. The crust is estimated to be several feet thick. During a burp, the force of the event is strong enough to physically disrupt the crust and allow the gas to escape. The top portion of the crust layer probably dries out between the events. It has been postulated that the crust is a foamy mixture of liquid, solids, and gas.
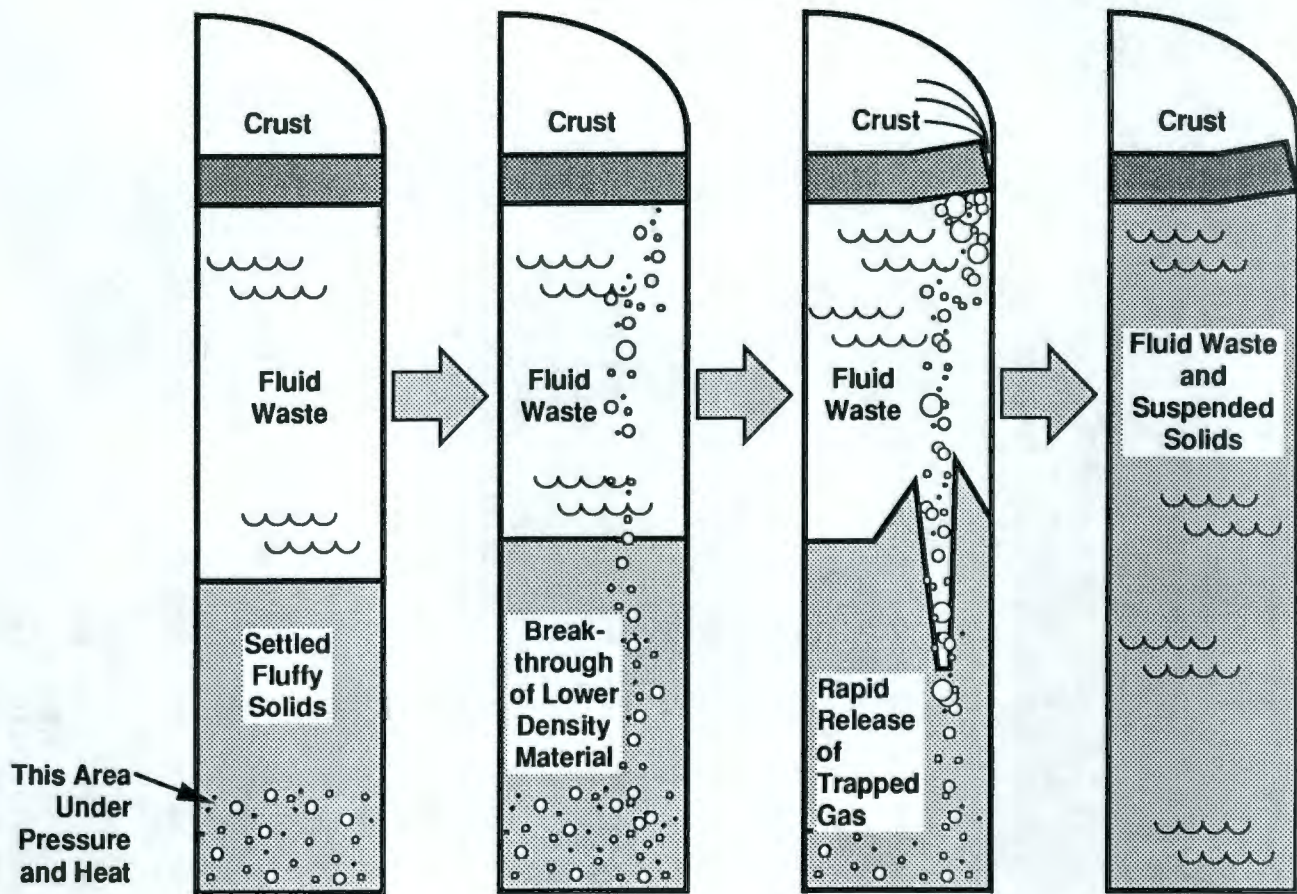
Figure 17. Postulated Mechanism of Tank 241-SY-101 Venting.

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5.2 THERMOCHEMICAL DEGRADATION

5.2.1 Background Information

All of the gases released from Tank 241-SY-101 have been observed in a series of studies that utilized synthetic double-shell slurry wastes in the absence of radiation. Gases that have been observed include N_2O and H_2, the most important gases from a safety aspect, as well as N_2 and minor amounts of CO, CO_2, CH_4, NH_3, and NO_x. While significant progress has been made in determining the chemical reactions responsible for generating these gases, it must be emphasized that the wastes in Tank 241-SY-101 are quite complex and that much work remains to be done.

The stoichiometry and rate of gas generation from synthetic wastes has been found to depend on waste composition, most notably nitrite, hydroxide, aluminate, and organic concentrations as well as organic identity. Delegard (1980) reported that gas generation occurred with HEDTA but not EDTA. The difference between these two chelating agents is that one of the carboxylate groups (-COOH) of EDTA is replaced by an alcohol group (-CH_2OH). Jansky and Meissner (1984) found similar behavior, reporting significant hydrogen generation when HEDTA and/or glycolic acid (hydroxyacetic acid) was present, but no gases generated in their absence. Delegard (1980) found that elimination of sodium aluminate from the synthetic waste composition substantially reduced the overall gas generation rate. This was recently corroborated by Ashby (1991). A first-order dependence on the hydroxide ion for concentrations below 1.5 M was also reported (Delegard 1980). In these studies, wastes containing no sodium aluminate or no sodium nitrite were found to generate only very small quantities of gas; elimination of oxygen also drastically reduced gas generation rates. Elimination of sodium nitrate actually enhanced the rate of gas generation.

Chemical mechanisms responsible for the generation of gases are not well understood at this time, but considerable progress is being made. Reaction of a nitrate ion with sodium aluminum hydroxide dihydrate in the presence of HEDTA to form a nitro-hydroxyaluminum-HEDTA complex has been described (Tank Waste Science Panel 1991), which leads to the formation of N_2O, H_2, CO_2, and ED3A. A series of mechanisms that may be responsible for the breaking of carbon-carbon and carbon-nitrogen bonds, and the formation of hydrogen, ammonia, and other products have been described by Ashby (in Strachan 1991). The Oppenauer oxidation mechanism can also be used to explain the reaction of HEDTA via an intermediate hydroxyaluminum complex to form H_2. Cannizzaro-type reaction mechanisms have also been proposed as a means of generating H_2. Verification that these or other mechanisms are correct is being pursued through careful identification of reaction products by NMR and other methods, and through the use of isotopic labels to show the source of the product gases.

5.2.2 Comparison to Gas Generation in Tank 241-SY-101

No clear agreement at this time among the synthetic waste studies exists as to the stoichiometry of gases generated from synthetic wastes, particularly for N_2O/H_2 ratios. At least some of this behavior probably arises from the

choice of experimental waste compositions and reaction temperatures. While N_2O exceeded the concentration of H_2 by more than a factor of 10 in the presence of sodium nitrite, H_2 exceeded N_2O concentrations by more than a factor of 6 in the absence of sodium nitrite (Delegard 1980). Jansky and Meissner (1984) also found H_2 concentrations to exceed that of N_2O by more than a factor of 10 when sodium nitrite was present. In contrast to these results from synthetic waste studies, gas compositional data obtained from the October 24, 1990 event indicate that N_2O and H_2 were present in approximately a 1:1 ratio (Barker 1991; Allemann 1991). It should be noted that the temperatures used in synthetic waste studies to accelerate the rates of reaction using small batches of synthetic waste are usually 100 °C or greater, whereas actual tank temperatures are approximately 60 °C; this difference may have a substantial impact on the stoichiometry of gaseous products. At Argonne National Laboratory, studies conducted at room temperature showed that no gases were formed in the absence of radiation. However, non-negligible generation of H_2 was detected by the same workers at 60 °C in the absence of radiation.

The quantity of hydrogen generated by thermally driven chemical degradation reactions in synthetic wastes accounts for perhaps one-third of that generated in the actual tank. A comparison of gas production calculated on the basis of synthetic waste studies and estimates for Tank 241-SY-101 is included in Table 8. Hydrogen generation rates from synthetic wastes of 0.0013 moles over a period of 500 h at 90 °C using a 500-mL waste volume correspond to a rate of approximately 500 moles of hydrogen per day per million gallons of waste. Using an activation energy of 25 kcal/mole (Delegard 1980; Siemers, in Strachan 1991) to adjust this rate to the actual tank temperature of 60 °C, a rate of 20 moles of hydrogen per day per million gallons of waste is obtained. Obviously, this estimation is very sensitive to the activation energy used. A change in the activation energy by 1 kcal/mole (to 24 or 26 kcal/mole) would alter the estimated hydrogen yield by nearly a factor of 5 at 60 °C. A similar treatment of preliminary N_2O results from work being conducted by Pacific Northwest Laboratory leads to an estimate of 100 moles of N_2O per day per million gallons of waste at 60 °C. This quantity is approximately twice the estimated rate of generation of this gas from the actual tank.

Experiments conducted at Argonne National Laboratory found an overall rate of gas generation from a reference synthetic waste composition of 0.13 mL/h per 100 mL waste volume at 120 °C. Correcting that gas volume to 60 °C using an activation energy of 25 kcal/mole yields a gas production rate of 55 moles of gas per day per million gallons of waste.

It must be emphasized that the above discussion is an estimate only of the quantity of gases that might be produced by thermally driven degradation reactions. Synthetic wastes used in these experiments were considerably less complex than actual wastes; speciation of the organic components in the actual waste has not been performed to date. To accelerate the rate of gas generation in the synthetic waste studies, reaction temperatures in the range of 90 to 120 °C were used rather than the actual tank temperature of 60 °C, requiring correction of the laboratory data to account for the activation energy. If such an estimation is to be valid, one must be certain that the reaction mechanisms do not change over the temperature range in question.

Table 8. Comparison of Gas Generation in Synthetic Waste Studies
with Estimates for Tank 241-SY-101.

	Moles H_2/day	Moles N_2O/day	Comments
Thermochemical	20	100	Results at Pacific Northwest Laboratory were obtained at 90 °C and corrected to 60 °C using an activation energy of 25 kcal/mol
Radiolytic	21	207	From studies at Argonne National Laboratory
Estimates for Tank 241-SY-101	64	52	Based on a slurry growth rate of 0.11 in./day (Strachan 1991) and vent gas analyses for the October 24, 1990 event.

The cause for the discrepancy between N_2O yields estimated from synthetic waste studies and that estimated from actual tank data is not known. Gas releases from Tank 241-SY-101 have been found to contain approximately equimolar quantities of N_2O and H_2, while synthetic waste results generally show N_2O to be present at concentrations 6 to 10 times greater than H_2. Considerably more N_2O production is estimated from synthetic waste studies than is indicated by actual release data. One possible explanation involves the solubility of N_2O, which is orders of magnitude greater than that of H_2. This high solubility may provide a means for enhanced transport of this gas through the liquid relative to H_2 and greater continuous release rates from the tank surface. Monitoring of N_2O and H_2 releases from Tank 241-SY-101 between release events would be valuable in establishing whether the above is important.

5.3 GAS GENERATION DUE TO RADIOLYTIC PROCESSES

5.3.1 Background Information

The gases H_2 and O_2 are produced by the radiolysis of water, but when the chemicals present in Tank 241-SY-101 are added, the yields of these gases are markedly altered, and other gaseous products result. In addition to H_2, N_2O and N_2 were also found. Oxygen has been observed in the absence of organic solutes but is consumed if organics are present. Other gases that are likely to be produced are NH_3 and CO_2.

Other radiolysis products may be important in gas generation. Degradation products of the organic chelators may be important in thermal reactions. For example, the degradation product formaldehyde (and other molecules with C-H bonds that are not in the α position to a carbonyl group) have been proposed as sources of thermally produced H_2. Evidence exists that hydrogen peroxide, which is formed in the radiolysis of water, can also form hydrogen in simulated tank systems.

Hydrogen and N_2O are of principal importance with respect to Tank 241-SY-101. The sources of hydrogen in radiolysis are well known for aqueous solutions containing no organic material. Hydrogen can be formed by the direct dissociation of water as well as by reactions between the primary transient species $H^\cdot$ and the solvated electron (e_{aq}^-). Because of the nonhomogeneous nature of energy deposition by ionizing radiation, which results in very large local concentrations of these transient species, the latter reactions cannot be reduced to zero at attainable concentrations of scavengers. Direct dissociation of water cannot be affected by added scavengers. Nevertheless, concentrations of NO_2^-, NO_3^-, and OH^- similar to those present in Tank 241-SY-101 do cause great reduction in the radiolytic yield of H_2, and the effects of variation in the concentrations of these ions on the H_2 yield can be predicted. The presence of organics causes an increase in the yield of H_2 due to the reaction of $H^\cdot$ atoms to abstract $H^\cdot$ from the organic, but the magnitude of this increase is limited by the aforementioned inorganic ions, primarily nitrite ions, that effectively compete for the $H^\cdot$ atoms. The effects of other solutes on the H_2 yield can be predicted if the reactivity of the solute with $H^\cdot$ atoms is known at high pH. Prior knowledge concerning N_2O is much less complete compared with H_2, and the exact mechanism of N_2O formation is not known; information given in Section 5.3.2 summarizes that state of knowledge.

5.3.2 Comparison to Gas Generation in Tank 241-SY-101

Modeling calculations have been performed and experiments conducted at Argonne National Laboratory using a homogeneous, simulated waste solution. The radiolytic yields (G-values in molecules/100 eV of energy deposited) of gases produced were determined. Yields of H_2 and N_2O have been measured in solutions irradiated at 30 and 60 °C that contain 2.12 M NaOH, 1.30 M $NaAlO_2$, 2.22 M $NaNO_2$, and 2.79 M $NaNO_3$ (a solution intended to mimic the tank solution and referred to as solution "P" below), and concentrations of various organics (e.g., EDTA, HEDTA, IDA) in the range of 0.1 to 0.2 M. Nitrogen and O_2 were also determined, but N_2 was generally not detectable (see below) and the addition of organics reduced a small $G(O_2)$ from solution P to zero. In fact, O_2, initially present in test solutions, is consumed when organics are present. The other likely gaseous products that have not yet been confirmed or denied are NH_3 and CO_2.

The dependence of the yield of H_2 on the organic material should depend on the concentration and reactivity of the H atom with the organic material. In line with this finding, the G-values of H_2 show a qualitative correlation with the number of C-H bonds in the additive and a linear dependence on organic concentration. The G-values of H_2 and N_2O are somewhat higher at the higher temperature. For H_2, the increase is in the range of 40 ±30% for a variety of additives and conditions. The variability in yield could be due to

differences in activation energy for the hydrogen abstraction reaction. For N_2O, the increases at 60 °C are somewhat larger and generally fall in the range of 25% to 100%. Because 60 °C corresponds to the approximate temperature in Tank 241-SY-101, the G-values of H_2 and N_2O measured at 60 °C will be discussed in the following paragraphs, unless otherwise noted.

Independent of dose or dose rate, the generation of H_2 occurs with a G-value in the range .02 to .07 from solution P containing concentrations of the organic chelators and their degradation products chosen to simulate Tank 241-SY-101 wastes. This estimate of G-value is based both on G-values measured when well-controlled additions of organic chelators were made and the G-values measured on a solution that had been pre-irradiated to simulate the effects in Tank 241-SY-101. Nitrogen was observed with a G-value of 0.13 from pre-irradiated material, but N_2 was not detected from radiolysis of other simulated waste solutions. Generation of N_2O from solution "P" with added organics occurs much more efficiently, having a G-value of about 1, a yield which does not appear to depend on dose or radiation intensity.

From these yields, H_2 and N_2O generation rates of 2.5×10^{-9} and 3.6×10^{-8} moles liter^{-1}min^{-1}, respectively, are determined for synthetic Tank 241-SY-101 wastes. A nonradiolytic yield of H_2 at 60 °C of 1.3×10^{-9} moles liter^{-1} min^{-1} has been observed in solution P containing 0.17 M IDA; this yield brings the total rate of H_2 generation up to 3.8×10^{-9} moles liter^{-1}min^{-1}. Of course, application of these numbers to the tank is an approximation both because it is not clear that this approach is applicable to nonhomogeneous phases, and because only the approximate chemical composition of the material in the tank is known; specific organic species present in the waste are unknown. The yield of hydrogen will be strongly dependent on the organic and NO_2^- concentration but only weakly on the NO_3^- concentration.

From the above measurements, yields of 21 moles/day of H_2 and 207 moles/day of N_2O are predicted (see Table 8). To explain the quantity of H_2 generated per day based on slurry growth data, a H_2 production rate of approximately 64 moles/day and a N_2O production rate of 52 moles/day are needed. Thus, the measured production rates lead to about one-third the H_2 production observed and about four times the N_2O observed. Whether the radiolytic yields from the nonhomogeneous phases are sufficiently different to explain these disparities remains to be determined. Hydrogen production from organic radicals catalyzed by particulates as a possibility.

The large N_2O excess has not been explained from experiments done on homogeneous systems where the total dose is not sufficient to saturate the solutions in N_2O or H_2. One can speculate on physical or chemical mechanisms to explain the discrepancy. A physical mechanism whereby N_2O is continually lost between release events at a much larger rate compared with H_2 is conceivable. Such a speculative mechanism follows. If N_2O is adsorbed much more strongly than H_2 on particulate matter, a release event may not appreciably dislodge N_2O relative to H_2. Then, N_2O generated after a release event would escape at a rate closer to its production rate because its adsorption sites would still be saturated, whereas the H_2 would be less likely to escape in this way because its adsorption sites would have been purged of H_2 during the release event. A similar variant would be that the N_2O is much less strongly bound, or not bound at all to the particles so that almost all

of the N_2O escapes during the time between events. This means that the gas measured in an event does not well reflect the total yield of the gas. Another alternative is the chemical reaction of the N_2O with radicals and ions (e.g., NO_3^{2-} produced in the solution). A saturated solution of N_2O in solution P is approximately 1 M, so radical lifetimes in the millisecond range would make such a mechanism possible. While no evidence exists in the experimental yields of N_2O as a function of total dose, insufficient dose has been given to test samples to create sufficient N_2O to saturate the solution.

Some information related to the mechanism of N_2O formation has been obtained. Use of sodium glycolate as an organic additive still results in a substantial yield of N_2O despite the fact that there is no nitrogen in glycolate. Also, the use of ^{15}N-labeled glycine as an additive results in N_2O that contains a negligible amount of ^{15}N. These observations show that the nitrogen originates from the inorganic constituents, even though the organic is necessary to produce N_2O.

6.0 CONCLUSIONS

The knowledge and understanding of the risks from the cyclic ventings of Tank 241-SY-101 have been greatly enhanced because of the sampling and laboratory studies conducted in fiscal year 1991.

Additional instrumentation for evaluating the composition of the vented gases has led to an estimated composition that is mainly hydrogen, nitrogen, and nitrous oxide. Small amounts of ammonia and water vapor are also present. The concentration of hydrogen in the exhaust header on top of the tank is above the lower flammability limit in some of the gas release events, but it is at that value for only a short time. The total amount of gas released in these episodic events ranges from 3,000 to 9,600 ft^3. Similarly, the observed changes in the surface level of the waste range from 5 to 10 in. During a gas release event, the hotter waste from the bottom portion of the tank moves to the top; this movement has been postulated to be due to a density instability that results from the entrainment of the gas.

A major effort was initiated to understand the mechanisms that are involved in the production of the various gases. Studies are being conducted on synthetic waste mixtures to determine the radiolytic mechanisms for the production of hydrogen and nitrous oxide. These studies have shown that the H_2 and N_2O are produced in the synthetic wastes that contain various organic compounds, but the production rates do not match those inferred from the analysis of the gas release events. Laboratory studies are also being conducted to evaluate the production of gases by the thermochemical degradation of the various chelating agents. These organic compounds have most likely degraded into numerous (ca. 100) compounds, thus presenting a very complex mixture. Tests are being done to determine the amount and composition of gases produced as a function of time at various temperatures. Both Oppenauer oxidation and Cannizzaro reaction mechanisms may be involved in the formation of hydrogen.

In fiscal year 1992, the laboratory studies on the gas generation mechanisms will continue, and studies will also be conducted to gain insight on the processes responsible for gas retention and release.

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